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ERRATA:

Page.	Line.	for	Read
119	31	1937	1917
121	8	in Table I	in Table II
"	12 (Table I)	10	1.0
126	"	amylse	amylase
282	2*	Armstrong	Joshi & Sane
283	2*	then filtered The filtrate	then filtered The residue was then treated with hot alcohol and filtered The filtrate etc.
"	6*	11.38	11.50
284	5	-5-iodo-7-amino	4-iodo-6-amino
404	9*	5-iodo-,	4-chloro-6-amino
479	Table I (contd) No. 17 & 18		17. Copper bispyridine thio- cyanate $[\text{Cu}(\text{C}_5\text{H}_5\text{N}_2)(\text{SCN})_2]$ and 18 Copper cystin $[\text{Cu}(\text{C}_6\text{H}_{10}\text{O}_2\text{C}_4\text{S}_2)] \cdot 2\text{H}_2\text{O}$
489	para 2, 4		Read "after 141°."

"It contained chlorine and the hydroxy group. (Found: Cl, 44.12. $\text{C}_{12}\text{H}_6\text{O}_2\text{Cl}_4$ requires Cl, 43.83 per cent). Chlorine in the side-chain was also estimated as AgCl. (Found: Cl, 33.23 $\text{C}_{12}\text{H}_6\text{O}_2\text{Cl}_4$ requires Cl, 32.87% (assuming that all the hydrogen atoms in the side-chain have been replaced by chlorine). When the alkaline solution was acidified with dilute nitric acid a solid was obtained. It showed the presence of hydroxy and carboxy groups. It contained chlorine."

5765 728

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From Bottom.

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1948

PRESIDENTIAL ADDRESS*

By PROF. P. RÂY

PART I. MEDIUM OF INSTRUCTIONS FOR SCIENTIFIC SUBJECTS

It is well known that the function of a scientific society like ours consists primarily in the exchange of informations and ideas among workers in the same field. This is the way in which science has grown and science can grow. The imposing edifice of science is being built up upon the accumulated knowledge of the past. It is, therefore, necessary that the facts discovered and ideas developed in all lands at all times should be available to all workers in science. The publications of various scientific societies serve mainly as agents for this purpose. An Annual General Meeting of the Society, therefore, offers an occasion on which we can take stock of our achievements and activities in this direction, and discuss the extent to which we have succeeded in exercising this function. A dispassionate analysis of the quality and quantity of papers published in our Journal, however, reveals little justification for complacency or encouragement. Now that India is a free nation, a great responsibility has devolved on us in claiming her rightful position in the scientific world—a sacred task for which we shall have to prepare ourselves so that we may deserve what we aspire after. Looking back to the distant past of India's history, we find that India's contribution in arts, literature, philosophy and science was in no way inferior to that of any of her contemporary nations, if not actually better. It is now an acknowledged fact that India's past achievements in arts, literature and philosophy were of the highest order, and have drawn unstinted admiration and reverence from the best of our modern thinkers. In practical sciences too, I shall refer here only to chemistry in which we are interested, her contributions were far ahead of the time. The famous wrought iron pillar at Delhi near Kutab, believed to have been constructed in the 4th century A.D., which has wonderfully withstood the onslaught of rain and air for over fifteen centuries, numerous iron beams and clamps of very large dimension in the temple of Bhubaneswar and at Konarak (600-900 A.D.), huge iron girders in the temple of Puri (1174 A.D.), the solid copper bolt in the Rampura Asoka pillar near Nepal, believed to be a product of the 3rd century B.C., the huge copper statue of Buddha weighing about 1 ton found at Sultangunge in Bhagalpur and believed to be a product of the 5th century A.D., are but a few of the numerous evidences of the remarkable skill displayed by the early Indians in large scale metallurgical and metal work, inspite of poor appliances at their disposal at the time. In the field of preparative chemistry reference may be made to the preparation of *mridu kshara* or mild

* Delivered at the Twentyfourth Annual Meeting of the Indian Chemical Society, 1948.

alkali (carbonate) and *tikshna kshara* or caustic alkali so meticulously described in the Ayurvedic treatise *Susruta* as early as the 5th century B.C. These methods are characterized by such a high degree of perfection that they can be bodily transferred to any modern text-book of chemistry. While recalling these glorious achievements of our forefathers in distant ages we cannot overlook the fact that as soon as India lost her freedom she practically sank into a dark age with absolutely no record worthy of note regarding her activities in experimental sciences, and, as the late Sir P. C. Ray very painfully but appropriately puts, "her name was all but expunged from the map of the scientific world". From this intellectual torpor there has, however, been an awakening from the beginning of the present century, and while India regains her freedom to-day it becomes a bounden duty for every one of us to put forth his best to revive her ancient glory, so that we may claim for her once again a rightful position in the scientific world and prove ourselves worthy of our great cultural heritage.

I cannot but refer here to a matter with which we, as scientists, are vitally interested, and with which the scientific progress and welfare of the country are intimately associated. You are all aware that with the dawn of freedom in our country there has been a popular demand for changing the medium of instructions in our universities from English into the language of our own country, and the Governments of many provinces have already adopted the provincial vernacular as their Court language. This is quite natural and is as it should be from the nationalistic point of view. But fortunately or unfortunately in India many things, which are quite natural and obvious in other countries, assume a somewhat different and complicated aspect from the viewpoint of her national growth and national welfare, because of her unusual geographical position, her colourful past history, variety of her provincial languages, and diversity of her population and their habits of life. That instruction in a foreign language in schools, colleges, and universities is not only absurd and unnatural, but positively detrimental to understanding and progress, involving an unnecessary and huge waste of time and energy, needs no discussion. But the question is what should be the medium of instruction in different provinces of India. If each province adheres to its own provincial language as it naturally does even up to a certain standard now, a considerable difficulty would be experienced in inter-provincial cultural intercourse and administrative activities. Migration of students from one provincial university to another, selection of teachers from one province for another, recruitment of officers and specialists for central public services will be associated with enormous difficulties, if not altogether inoperative and unpracticable. If a national *lingua franca* for the entire Indian dominion be adopted, as is suggested, which may be Hindi or Hindusthani, then, in addition to each provincial language, the national language should also be made compulsory for every stage of our education. Besides, if we are to keep ourselves in touch with the cultural flow of Europe and America, we shall have to retain English as a compulsory second language in all our colleges and universities; otherwise, we would isolate and cripple ourselves both intellectually and culturally. All these difficulties are sure to multiply manifold in the case of scientific subjects with their characteristic terminologies and symbols. Imagine the way in which we shall have to carry out our discussion in all-India

scientific gatherings like Indian Science Congress Sessions, the National Institute of Sciences of India, and the various All-India Scientific Societies like ours. What will be the character of our organ, the Journal of the Indian Chemical Society, and, for the matter of that, of all other similar scientific journals now published in India? If workers of different provinces send in their contributions in their own provincial languages and scripts, it will create not only serious difficulties in their printing and publication, but will defeat the very purpose of such journals, which, as has been stated above, aims at a free and unfettered exchange of informations and ideas for the progress of science. It may, however, be argued that the publications will be made only in the *lingua franca* of India and in a script of its own with common terminologies. Then again, it has to be considered whether under such altered conditions we shall be able to maintain our exchange relation with the learned societies of Europe and America undisturbed, and whether our publications will receive due notice in the Abstracts of foreign countries, which is so essential to our activities and progress. I am afraid, it will be too much to expect such recognition from abroad unless our contributions attain such a high standard as to compel the foreign scientists to look for light and guidance from us. We shall thus be cut off and isolated from the scientific progress of the world, which we certainly do not desire.

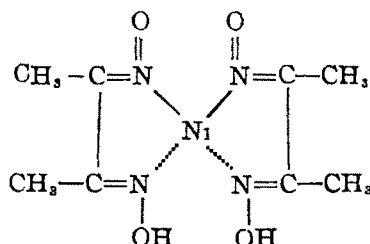
I have rather dwelt at some length on this problem as I consider it to be of fundamental importance to our national welfare, our scientific progress and social advancement. The problem, as I have shown, cannot be solved province-wise. It is an all-India problem and should be thoroughly discussed in All-India Organizations. First of all, the various All-India Scientific Societies should discuss this problem in their individual organizations and communicate their considered opinions to the Indian Science Congress Association and the National Institute of Sciences of India. The representatives of these two bodies, after the matter has been discussed in their respective organizations with due consideration of the opinions of the All-India Scientific Societies, should then meet together along with one representative each of these Scientific Societies for a final recommendation on the subject to the Government of the Union. All attempts to provincialize the scientific terminologies and symbols should be discouraged. That will lead only to disintegration and confusion, while science aims at integration. What is required is a dispassionate consideration of the problem free from sentiment, pride and prejudices.

PART II. STEREOCHEMISTRY OF NICKEL, COPPER AND SILVER

I shall now proceed to the scientific portion of my address as I do not like to be guilty of the violation of a wholesome convention for the President of your Society. I have, therefore, chosen to speak to-day on the stereochemistry of nickel, copper and silver in which I have been interested for some time.

From a consideration of the physical and chemical properties of the co-ordination compounds chemists distinguished them long ago into two classes; *viz.*, perfect or

strong, and imperfect or weak complexes. Those, which are unstable or dissociate readily in aqueous solution, are regarded as weak or imperfect complexes, and the stable ones, whose dissociation in aqueous solution is negligible, are placed in the group of strong or perfect complexes. As no sharp line of demarcation could be drawn between these properties, they assumed that the two classes merge insensibly into each other, and the transition between them is a *continuous* one. As an illustration, we may cite here a number of complex nickel compounds, such as potassium nickelocyanide, $K_2[Ni(CN)_4]$, nickel dimethyl glyoxime,



nickel ethylenediamine thiocyanate, $\left[\text{Ni} \left(\begin{array}{c} \text{CH}_2 - \text{NH}_2 \\ | \\ \text{CH}_2 - \text{NH}_2 \end{array} \right)_2 \right] (\text{SCN})_2$, nickel tetrammine

sulphate, $[\text{Ni}(\text{NH}_3)_4]\text{SO}_4$, etc. The first two substances, potassium nickelocyanide and nickel dimethylglyoxime, belong to the group of perfect complexes, as they are not attacked by the usual reagents for nickel, like caustic alkali, sulphuretted hydrogen, etc. The last two, nickel ethylenediamine thiocyanate and nickel tetrammine sulphate, give at once a precipitate of nickel sulphide on treatment with hydrogen sulphide; they also give a precipitate of nickel hydroxide with caustic alkali. These substances should, therefore, be viewed as imperfect complexes. A determination of the concentration of free nickel ions in their equivalent solutions lends further support to this view. This naturally raises the question about the nature of the bond in co-ordination complexes. With the development of the electronic theory of valency two different views were advanced in order to elucidate this point. Kossel (*Ann. Physik*, 1916, **49**, 229), in accordance with his theory of chemical combination as due to electrostatic attraction between oppositely charged particles, suggested that in the formation of co-ordination compounds also a similar electrostatic attraction should play the main role. Hence the bonds between the central atom and the co-ordinated units are of the polar type, or ionic in character. On the other hand, Lewis (*J. Amer. Chem. Soc.*, 1916, **38**, 762), Langmuir (*ibid.*, 1919, **41**, 868) and Sidgwick (*J. Chem. Soc.*, 1923, **123**, 725) hold that the bonds in the co-ordination complexes are of the non-polar or covalent type, due to the sharing of a pair of electrons per bond, donated by the co-ordinated units to the central atom. Neither of these views can obviously account for the properties of all types of complexes. That in some of the complexes the bonds are predominantly of the non-polar type was more or less definitely established by the classical work of Werner on co-ordination complexes, leading to the isolation of isomeric and optically active compounds. A deter-

mination of the magnetic properties of a large variety of complex compounds led the present speaker (*Z. anorg. Chem.*, 1928, **174**, 191) to classify the co-ordination complexes into two distinct types, polar and non-polar, the transition between which must be a *discontinuous* one. In the polar class the bonds are believed to be ionic, and in the non-polar they are supposed to be covalent. Referring to the series of nickel complexes cited above, potassium nickelocyanide and nickel dimethylglyoxime were found to be diamagnetic, while the other two showed paramagnetism, practically identical with that for nickelous ion. In order to account for the striking change of magnetic properties in many of these non-polar co-ordination compounds, it was suggested that such changes were usually associated with the more or less complete filling up of the $3d$ -orbital of the central atom with electrons in the case of the elements of the first transitional group. In other words, in those cases where the electrons supplied by the co-ordinated units during the bond formation enter the inner d -level of the central atom, leading thereby to a coupling of the unbalanced electrons originally present in the atom, a profound alteration in the paramagnetic properties of the atom will result. The two types of complexes were, therefore, termed *penetration* and *associated* complexes. In the latter, it is regarded that the bonds are either ionic, or the electrons of the co-ordination bonds avoid entering the inner d -level. This is in fairly good agreement with the view developed by Pauling on the basis of quantum mechanics in his well-known and comprehensive theory of co-ordination compounds, which relates the nature of the bond orbitals with the spatial configuration of the molecules, and has thus provided a theoretical basis for stereochemistry (Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367; cf. also "The Nature of the Chemical Bond", 1940). According to this view, hybrid bond orbitals formed by the linear combination of s - and p -orbitals of the valency shell with one or two d -orbitals of the penultimate valence shell are of special significance in accounting for the configuration of the co-ordination compounds of the penetration type. Four strong equivalent hybrid d^3p^3 bond orbitals lead to a planar square configuration of the four-coordinated complexes; similarly six strong equivalent hybrid d^2sp^3 bond orbitals give rise to a regular octahedral configuration of the co-ordinated units around the central atom. This, in fact, provides a theoretical justification of Werner's theory regarding the configuration of complex compounds, which was placed on a solid foundation by his own classical work. On the other hand, four equivalent hybrid sp^3 bond orbitals or sp^2d bond orbitals, formed with orbitals of the same valency shell, have been shown by Pauling to give rise to a tetrahedral and planar square configuration respectively for four-coordinated complexes of the associated type. The octahedral complexes of the associated type similarly result from the use of six equivalent hybrid sp^3d^2 bond orbitals, derived from the same valence shell. The bonds in these associated complexes, as their electronic configurations show, may resonate between the covalent and the ionic type. A consideration of the electronic configurations of the nickel, copper and silver complexes makes it clear, and enables us directly to deduce the magnetic moment of their central atoms on the basis of Bose-Stoner's formula:

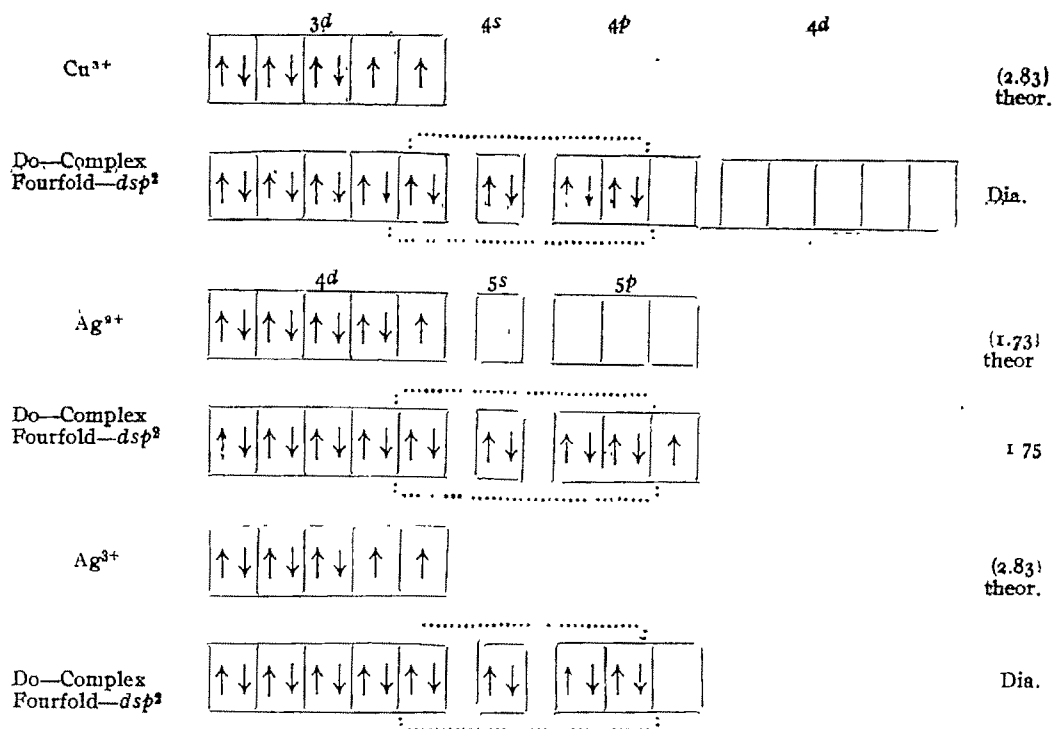
$$\mu_r = \sqrt{4S(S+1)} ;$$

where S = the resultant spin moment. Conversely, a knowledge of the magnetic moment

of a co-ordination complex can, in many cases, reveal the nature of the bond involved in its formation and disclose the structure of the molecule itself.

Electrons in Ions and Co-ordination Complexes.

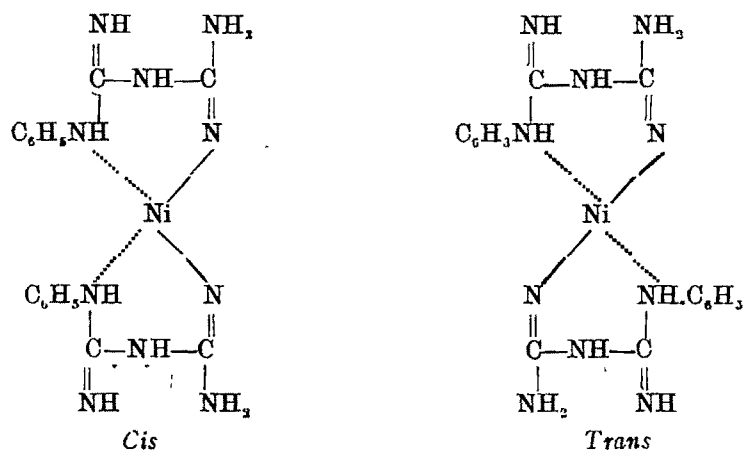
	3d	4s	4p	4d	μ_B (obsv.).
Ni^{++}					2.8—3.2
Do-Complex Fourfold— sp^3 or sp^3d					2.8—3.0
Do— dsp^3					Dia.
Do-Complex Sixfold— d^2sp^3					3.0
Ni^{++}					(4.9) theor.
Do-Complex sixfold— d^2sp^3					Dia.
	3d	4s	4p	4d	μ_B (obsv.).
Cu^{++}					1.95—2.0
Do-Complex Sixfold— sp^3d^2					1.84
Do-Complex Fourfold— sp^3 or sp^3d					1.86—1.94
Do— dsp^3					1.73—1.84



The octahedral configuration for the six-covalent co-ordination complexes of many transitional elements was suggested and proved by Werner from a consideration of their chemical and electrochemical behaviour, as well as by the isolation of isomers and the resolution of asymmetric bodies into optically active components. The determination of the crystal structure by the X-ray method in recent times of some compounds, containing octahedral complexes, provides the most direct confirmation of Werner's view in this respect.

In the case of four-covalent complexes, Werner as long ago as 1893 suggested co-planar configuration for bivalent palladium or platinum atoms in certain molecules, in order to account for the isomerism of compounds like $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. The planar configuration for $[\text{PdCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ ions in K_2PdCl_4 and K_2PtCl_4 has been subsequently established by the X-ray method. There was no definite evidence for planar configuration for 4-covalent complexes formed by elements like nickel, copper or silver, till Pauling developed his theory of complex compounds in 1931, as discussed above. It has now been shown that many diamagnetic complexes of bivalent nickel exist in two isomeric forms. These include nickel dimethylglyoxime (Tschugaeff, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1466), nickel benzylmethylglyoxime (Sugden, *J. Chem. Soc.*, 1932, 246), bithiosemicarbazide nickelous sulphate (Jensen, *Z. anorg. Chem.*, 1936, **229**, 265), which are readily interconvertible. The co-planar structure of nickel dithio-oxalate ion and nickel salicyaldoxime has been established by the X-ray method (cf. Cox, Wardlaw and Webster, *J. Chem. Soc.*, 1935, 459, 1475). Nickel phthalocyanine furnishes another instance of the kind (Robertson, *ibid.*, 1935, 615). Three different modifications of nickel phenylbiguanide also were isolated in our laboratory (Ray and

Chakrabarty, *J. Indian Chem. Soc.*, 1941, 18, 614). These differ in their colour, solubility and decomposition temperature, and are distinguished as α -, β - and γ -forms. The α -base is brick-red in colour, insoluble in water, but soluble in alcohol and acetone, changing rapidly into the yellow γ -variety. The same change occurs on keeping it in contact, or on heating, with water. It decomposes at 255° . The β -base is light yellow in colour, insoluble in water and all common organic solvents. On heating, it decomposes at 265° . The γ -form is deep yellow in colour, also insoluble in water and all organic solvents. It decomposes at 263° . From a consideration of the constitution of nickel phenylbiguanide it may be suggested that these possibly represent some of the various forms in which a molecule of this type is likely to occur, provided, of course, we do not attribute this difference in properties solely to polymorphism, for which, however, there is little justification. The α - and β -varieties were regarded as *cis*- and *trans*-isomer respectively as shown below :



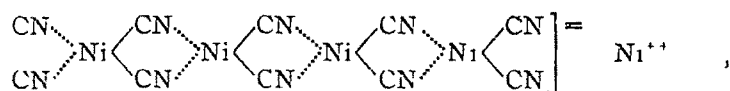
The *cis*-modification may again exist in two different forms; in one, both the phenyl groups would lie on the same side of the plane, while in the other, it would occur on the opposite sides. The latter, having no plane of symmetry, might again occur in two optically active forms.

A very interesting case of isomerism has been described by Lifschitz and co-workers (*Z. anorg. allg. Chem.*, 1939, 242, 97). This relates to the fourfold nickel complexes of stilbenediamine and monophenylethylenediamine. Each member of these two series of nickel complexes has been obtained in two different forms, yellow and blue. The former are diamagnetic, and the latter, paramagnetic like the simple nickel salts. They, therefore, represent respectively complexes of the penetration type, having square planar configuration with dsp^2 bonds, and of the associated type with tetrahedral sp^3 or square sp^2d bonds, resonating with ionic bonds. A glance at the electronic configuration of nickel complexes, given above, makes it clear. It is further significant to note that all diamagnetic fourfold nickel complexes, which belong to the penetration type, are yellow, orange, or red in colour; while all paramagnetic fourfold complexes, which are of the associated type, are blue or green in colour. This seems to suggest a relationship between the colour of the complex and the type of its structure and bond.

Octahedral bivalent nickel complexes with d^2sp^3 bonds should show a moment value due to two unpaired electrons promoted to the $4d$ -level. This is illustrated by the magnetic moment of nickel *tris*dipyridyl salts (Ray and Sen, unpublished).

On the other hand, a sixfold quadrivalent nickel, as in barium or ammonium nickel molybdate, has been found to be diamagnetic, and hence it forms six octahedral d^2sp^3 bonds. The composition of these complexes is rather unusual and is given by the formula, $3(\text{NH}_4)_2\text{O}(\text{BaO})\cdot\text{NiO}_2\cdot 9\text{MoO}_3\cdot x\text{H}_2\text{O}$. It is, therefore, suggested that they should be regarded as molecular compounds of 6-molybdenum and 12-molybdenum heteropolyacid salts, *viz.*, $\text{R}_{11}\text{H}_4[\text{Ni}^{\text{IV}}(\text{MoO}_4)_6]\cdot\text{R}_8[\text{Ni}^{\text{IV}}(\text{Mo}_2\text{O}_7)_4]$, or better as $\text{R}_6\text{H}_2[\text{Ni}^{\text{IV}}(\text{MoO}_4)_3(\text{Mo}_2\text{O}_7)_3]$, a new type of 9 molybdenum heteropoly complex salt (Ray *et al.*, *J. Indian Chem. Soc.*, 1948, 25 51). Alkali nickel periodates, $\text{K}(\text{Na})\text{NiIO}_6$, with tetrapositive nickel, recently prepared in our laboratory (Ray and Sarma, *Nature*, 1946, 627), have been found to give a very low magnetic moment value, about 1 Bohr magneton, which is even lower than that required for the presence of one unpaired electron. But, as is evident from the scheme of electronic configuration shown above, a quadrivalent nickel ion would have given a much higher moment value, about 5 Bohr magnetons. It is, therefore, concluded that the quadrivalent nickel atom is present in the crystal as the centre of a co-ordination complex and is surrounded octahedrally by six oxygen atoms, the bonds between the nickel and the oxygen atoms being predominantly covalent of the d^2sp^3 type. The compound in its crystalline state thus behaves as a penetration complex, though the molecular composition corresponds to a mixed alkali nickel salt of orthoperiodic acid.

Similar autocomplex formation in the solid state has been observed also in the case of some simple bivalent nickel compounds. Anhydrous nickel cyanide, for instance, gives a moment value of only $0.65 \mu_B$ (Ray and Sahu, *J. Indian Chem. Soc.*, 1946, 23, 161). It has, therefore, been suggested that the nickel atom in the crystal forms a planar square complex with the surrounding CN-groups by means of dsp^2 bonds, giving rise to a chain polymer as depicted below :



or $\text{Ni} [\text{Ni}(\text{CN})_{10}]$.

There are some sixfold copper complexes with the metal atom in the bivalent state. These may be regarded as belonging to the associated class either with octahedral sp^3d^2 bonds or ion-dipole bonds, or with bonds resonating between these two. Bivalent copper is not likely to form octahedral penetration complexes with their characteristic d^2sp^3 bonds, as there are not sufficient d -orbitals of the inner shell available for bond formation. For, this would require promotion of three electrons to a higher level, involving a considerable expenditure of energy. The configuration, therefore, indicates that the magnetic moment of these complexes remain practically unaltered from that of the simple cupric ion. This has been verified in the case of copper *tris*ethylenediamine and *tris*pyridine complexes, as well as for $\text{K}_2\text{Ca}[\text{Cu}(\text{NO}_2)_6]$ and similar salts (Ray and Sahu, *loc. cit.*).

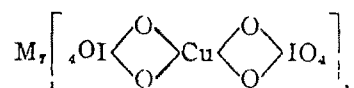
Bivalent copper like bivalent nickel is very prone to form fourfold complexes. All the fourfold copper complexes, that have been examined by the X-ray method, show a planar structure. These include compounds like $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{Py}$, copper acetylacetonate, copper phthalocyanine, copper salicylaldehyde, copper picolinate, etc. The isomorphism of copper methylethylglyoxime with the corresponding nickel compound is also an evidence for the planar structure of the former. We have already seen that in the case of fourfold nickel complexes, measurement of magnetic moments provided a very convenient and convincing method for distinguishing the complexes of the penetration type from those of the associated class, as the former are all diamagnetic and the latter give the same paramagnetic moment as the simple nickel salts. This, however, is not possible in the case of fourfold copper complexes. As their electronic configurations show that in both types of complexes there would remain one unpaired electron in the central metal atom as in a simple cupric ion. This will lead almost to the same moment value for all. Nevertheless, a small but measurable difference in the moment value for the two types of complexes might be expected in view of the difference in the position of the unpaired electron in the two cases. An examination of their electronic configurations would show that in the penetration complexes the unpaired electron occupies a higher level, $4p$; while it occurs as a $3d$ -electron in the associated type as well as in simple cupric ion. Pauling ("The Nature of the Chemical Bond", 1940, p. 121), in fact, suggested that the planar complexes should show a lower moment value than the tetrahedral ones, because of the greater quenching effect of the more unsymmetrical field of the attached groups upon the residual orbital moment of the electron. For, the moment of the cupric ion in solution is always higher than the theoretical value of $1.73\mu_B$ on the basis of Bose-Stoner's formula, indicating the presence of a residual orbital moment. But no evidence of a tetrahedral cupric complex has yet been obtained by the X-ray method. All the compounds examined show planar structure; consequently, the bonds involved are either of dsp^3 or sp^3d type, corresponding to the penetration and associated complexes respectively. Hence, if there be any lower moment value for the 4-covalent copper complexes of the penetration type, it would be more likely due to the fact that in these the lone electron being promoted to a higher level is less influenced by the nuclear field with the consequent increase in the perturbing and quenching effect of the field of the neighbouring atoms and ions on its orbital moment. A systematic and careful measurement of a large variety of fourfold cupric complexes in our laboratory seems to provide a method for dividing these complexes into two such groups. It has been found that the moment value for one group, particularly after θ -correction, lies near about $1.73\mu_B$, while that of the other group is very nearly equal to $2\mu_B$. The former, therefore, represents the complexes of the penetration type and the latter, those of the associated one.

It is, however, of some significance to note in this connection that all those 4-covalent bivalent copper complexes, which show a lower moment value of about 1.73 – $1.84\mu_B$, are either red, dark brown, greenish yellow, or deep blue in colour, while those, giving a higher moment value of 1.9 – $2.2\mu_B$, are all green, blue, or blue-violet in colour. To a certain extent a distinction can thus be made between the penetration and the associated complexes of bivalent copper merely from their colour.

Notwithstanding their planar configuration, there is little definite evidence of geometrical isomerism among the 4-covalent copper complexes. Pfeiffer and Glaser (*J. prakt. Chem.*, 1939, *ii*, **153**, 265) have described two modifications of naphthaldehyde methylimine copper, one forming dark brown needles of metallic lustre and the other consisting of green needles, the latter changing into the brown variety at 140° or on keeping under methyl alcohol at the room temperature. But both gave solutions of identical colour in pyridine. Pfeiffer and Krebs (*ibid.*, 1939, **155**, 77) have also isolated two forms of sodium and barium salts of copper salicylaldehyde phenylimine *p*-sulphonic acid, which differ in their solubility in solvents like glycol or glycerine. Whether the difference in these cases is due to dimorphism or *cis-trans* isomerism could not be decided by the authors. Two modifications of copper phenylbiguanide salts have also been prepared by us. The chloride, for instance, has been obtained in bluish violet as well as in brick-red crystals, the former changing into the latter at 101° in presence of steam, or in long contact with water. They differ in their melting point, solubility and rate of hydrolysis, but give identical absorption spectra in aqueous solution (Ray and Chakrabarti, *J. Indian Chem. Soc.*, 1941, **18**, 609). Recently, we have obtained two modifications of copper bisdiethylbiguanide, which differ markedly in their colour. One forms deep blue crystals and the other forms bright red needles (m.p. 199°), the latter changing into the blue variety in long contact with water, while the former changes into the latter at 160°. They are insoluble in water, but dissolve readily in alcohol and other organic solvents. In solution they give identical absorption spectra. As they both give almost the same but a low magnetic moment value of $1.98\mu_B$ only, they are both 4-covalent complexes of the penetration type. In view of their great difference in colour we are disposed to think that they do really represent a case of geometrical isomerism and are related as *cis-trans* isomers to each other.

A simple salt, *viz.* anhydrous cupric chloride, CuCl_2 , unlike its hydrated variety, also has been found to give a lower moment value of $1.73\mu_B$ and hence behaves like a 4-covalent penetration complex with dsp^2 bonds. Like anhydrous nickel cyanide and palladous chloride, it can, therefore, be represented as an endless, long-chained, polymeric molecule.

Some copper complexes with copper in the tervalent state, namely alkali copper periodate and tellurate, have been described by Malatesta (*Gazzetta*, 1941, **71**, 467, 580). They are diamagnetic and their composition is represented by the formula, $\text{M}_7\text{Cu}(\text{IO}_6)_2 \cdot x\text{H}_2\text{O}$ and $\text{M}_6\text{Cu}(\text{TeO}_6)_2 \cdot n\text{H}_2\text{O}$ respectively. Their diamagnetic character can only result from an electronic configuration corresponding to that for a 4-covalent penetration complex of bivalent nickel, as shown in the scheme above. Each copper atom in the molecule, therefore, forms four co-planar dsp^2 bonds with four oxygen atoms of two $(\text{IO}_6)^{5-}$ or $(\text{TeO}_6)^{6-}$ groups, as can be represented by the formula,



for the periodate.

Now dealing with the stereochemistry of the remaining element, bivalent silver like bivalent copper has been found to form 4-covalent planar complexes of the penetra-

tion type. They show the same moment value as the corresponding copper complexes, viz., $1.73 \mu_B$, appropriate to one unpaired electron. This is clear from their electronic configuration. Planar configuration for the bivalent silver picolinate has been verified by the X-ray method and by isomorphism with the corresponding cupric compound (Cox, *et. al.*, *J. Chem. Soc.*, 1936, 775).

Recently we have prepared in our laboratory a number of complex tervalent silver salts of ethylenedibiguanide with fourfold co-ordination (Ray and Chakrabarty, *J. Indian Chem. Soc.*, 1944, 21 47). They are diamagnetic and hence presumably possess an electronic configuration similar to that for a planar bivalent nickel complex of the penetration type, since a tripositive silver ion resembles the bivalent nickel ion in its configuration. Consequently, silver in its tervalent state forms co-planar bonds of the dsp^3 type in its fourfold complexes. The tervalent silver periodates and tellurates, described by Malatesta (*loc. cit.*), which are also diamagnetic like the corresponding copper compounds, should, therefore, be represented like these latter as 4-covalent complexes of the penetration type with a planar structure.

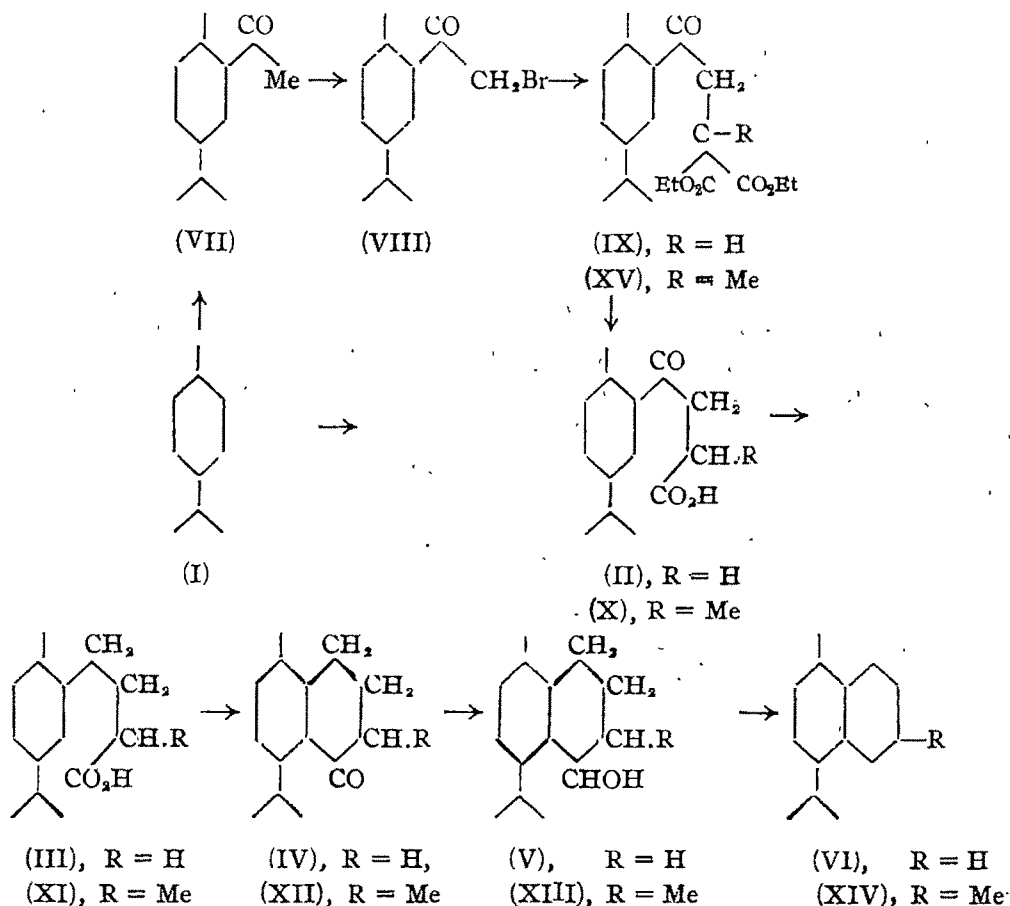
This concludes a brief review of the stereochemistry of the three common coinage metals; and it is really interesting to note that the modern and more refined physical methods have confirmed and placed on a sounder basis the views previously deduced by the classical methods of chemistry.

STUDIES IN SESQUITERPENES. PART I. A NEW SYNTHESIS OF CADALENE

By SUKH DEV AND P. C. GUHA

Cadalene and *apo*-cadalene have been synthesised by new and simpler procedures starting from *p*-cymene.

The succinic anhydride method ranks as an important synthetic tool amongst the various methods which are being employed in building up polycyclic hydrocarbons. Haworth and his co-workers used it extensively in the phenanthrene series (*J. Chem. Soc.*, 1932, 1125, 1784, 2248, 2717, 2720; 1934, 454). The method has also been used in the synthetic investigations on carcinogenic hydrocarbons (Cook *et al.*, *ibid.*, 1933, 398; 1934, 428; 1935, 767; 1938, 505; Adelson and Bogert, *J. Amer. Chem. Soc.*, 1937, 59, 1776, *et seq.*). The method furnishes sometimes a very convenient route to many alkyl naphthalenes which have been synthesised by rather complicated procedures (Heilbron and Wilkinson, *J. Chem. Soc.*, 1930, 2537; Ruzicka *et al.*, *Helv. Chim. Acta*, 1932, 15, 140; 1936, 19, 370, *et seq.*)



Cadalene, the important dehydrogenation product of some sesquiterpenes, was identified by Ruzicka and his co-workers as 1:6-dimethyl-4-isopropyl-naphthalene both by analytical and synthetic methods (*Helv. Chim. Acta*, 1922, **5**, 345, 369). The hydrocarbon has also been synthesised by various other workers (Barnett and Cook, *J. Chem. Soc.*, 1933, 22; Bardhan and Banerjee, *ibid.*, 1935, 476; Chatterjee, *J. Indian Chem. Soc.*, 1936, **13**, 588; Dutta, *ibid.*, 1941, **18**, 233). All these schemes involve steps from 7 to 11. The succinic anhydride synthesis is much simpler and is outlined above.*

In order to establish the conditions, succinic anhydride itself was employed in the first instance, 1-methyl-4-isopropyl-naphthalene (*apo*-cadalene) was thus synthesised. A number of independent syntheses of this is on record (Ruzicka and Migazzini, *Helv. Chim. Acta*, 1922, **5**, 714; Rapson and Short, *J. Chem. Soc.*, 1933, 128; Barnett and Cook, *ibid.*, 1933, 22).

p-Cymene is condensed with succinic anhydride or pyrotartaric anhydride in nitrobenzene solution in presence of anhydrous aluminium chloride to give the corresponding keto-acids (II, X). Since the substitution in the *p*-cymene ring nearly always occurs in the position 2 (*e.g.* acetylation, Claus, *Ber.*, 1886, **19**, 232), and also because methylsuccinic anhydride is known to react in such a way that the carboxyl group, furthest removed from the methyl, attaches to the aryl nucleus invariably (Klobb, *Bull. soc. chim.*, 1900, **iii**, **23**, 511; Oppenheim, *Ber.*, 1901, **34**, 4227; Haworth and Bolam, *J. Chem. Soc.*, 1932, 2248) the condensation products are expected to be of the desired structure. But in order to place the structures beyond doubt, the acids have been synthesised by straight forward methods. *p*-Cymene is acetylated to give 2-acetyl-*p*-cymene (VII) (Allen, "Organic Syntheses," XIV, p. 1). If this condensation is carried out in nitrobenzene instead of carbon disulphide, the yields are very much improved. A 70% yield is readily obtained instead of the 50-55% yields reported (*loc. cit.*). A change of solvents in such a condensation is known to alter the orientation sometimes (St. Pfau and Ofner, *Helv. Chim. Acta*, 1926, **9**, 669; Fieser, Holmes and Newman, *J. Amer. Chem. Soc.*, 1936, **58**, 1055; Chopin, *Bull. soc. chim.*, 1924, **iv**, **35**, 610). This product on oxidation with potassium hypobromite yields *p*-cymene-2-carboxylic acid, m.p. 71-72° (*cf.* Bogert and Tuttle, *J. Amer. Chem. Soc.*, 1916, **38** 1349). 2-Acetyl-*p*-cymene is brominated with one mole of bromine in dry ether to give the corresponding ω -bromo compound (VIII), the crude bromo compound is then condensed with the proper malonic ester to give (IX) or (XV). The esters, thus obtained, are hydrolysed with alcoholic sodium hydroxide and then decarboxylated at 180°-200° to give the keto-acids indistinguishable from the direct Friedel-Craft's condensation products.

The keto-acids are reduced by amalgamated zinc and hydrochloric acid, an immiscible solvent being employed (Martin, *J. Amer. Chem. Soc.*, 1936, **58**, 1438). The *p*-cymyl-2-acids (III and XI), so prepared, are obtained in good yields. In the case of γ -(*p*-cymoyl-2)-propionic acid, besides the normal reduction product (III), another product

* When this work had been completed and a preliminary note communicated to the *Science & Culture* in December 1946, a new synthesis of cadalene by Johnson and Jones appeared (*J. Amer. Chem. Soc.*, 1947, **69**, 792). Their synthesis is simpler than the previous syntheses but the present scheme still remains the simplest.

of m.p. 210-211° has been isolated which is insoluble in hot 20% aqueous potash. Huang-Minlon (*J. Amer. Chem. Soc.*, 1946, **68**, 2487) during the Clemmensen's reduction (Martin's procedure) of β -(*p*-phenoxybenzoyl)-propionic acid isolated a high melting byproduct for which he proposed the structure of the pinacol-dilactone. The product is insoluble in cold alkali. Similarly during the reduction of β -benzoylpropionic acid, a solid (m.p. 254°) has been isolated to which Fieser has given a similar structure ("Organic Syntheses", Vol. XV, p. 64). But since our product is insoluble in hot 20% aqueous potash, it is highly improbable that it is a lactone. The substance is under investigation.

The cyclisations of these acids to the corresponding tetralones (IV, XII) have been accomplished by the Friedel-Crafts intramolecular condensation of the acid chlorides. Ruzicka (*Helv. Chim. Acta*, 1922, **5**, 369) has reported the 2:5-dimethyl-8-isopropyl-tetralone-1 (XII) as a liquid, whereas our product soon crystallises out after distillation (m.p. 50-51°).

5-Methyl-8-isopropyltetralone-1 (IV) is reduced to the secondary alcohol (V) by sodium and absolute alcohol. But this reduction is carried out better by sodium in moist benzene. The 2:5-dimethyl-8-isopropyltetralone-1 (XII) is reduced in this way. Dimolecular reduction does not take place to any appreciable extent (cf. Ruzicka, *loc. cit.*)

The alcohol (V) is heated with selenium first at about 180°, when the evolution of the dehydration water practically ceases. The temperature is then raised to 280° and the dehydrogenation effected. 1-Methyl-4-isopropyl-naphthalene (VI) is isolated and characterised in the usual manner.

The alcohol (XIII), however, is first dehydrated with formic acid and then dehydrogenated with selenium to give cadalene (XIV).

EXPERIMENTAL

Syntheses of Keto-acids

(1) *2-Acetyl-p-cymene* (VII).—Anhydrous aluminium chloride (45 g., 1 mol.) was added in two lots to dry nitrobenzene (50 c.c.) placed in a three-necked flask and mechanically stirred. When the aluminium chloride had dissolved, the flask was cooled in an ice-salt mixture to 0°, when the aluminium chloride-nitrobenzene complex separated out. A mixture of *p*-cymene (43.7 g., 50.1 c.c., 1 mol.) and acetyl chloride (27.7 g., 25 c.c., 1 mol.) was then introduced in the reaction mixture dropwise during 45 minutes; the temperature was not allowed to rise beyond 10°. The flask was surrounded with more ice and the reaction mixture was left overnight (15 hours). Next day the reaction mixture, full of colourless crystalline addition product, was decomposed with ice and hydrochloric acid. The oil was extracted with ether, dried (Na₂SO₄) and the ether removed. The residue was carefully fractionated from a 250 c.c. modified Claisen's flask, when 40 g. (70%) of the product were obtained, b.p. 118-20°/9 mm.

2:4-Dinitrophenylhydrazone was prepared in the usual manner (sulphuric acid method) as yellow needles, crystallising in stais from petrol ether (75°-90°) containing 5% benzene, m.p. 137.5-138.5°. (Found: N, 15.58. C₁₈H₂₀O₄N₄ requires N, 15.72 per cent).

Acetylcymene (2.0 g. in 5 c.c. dioxane) was oxidised with potassium hypobromite and the 2-methyl-5-isopropylbenzoic acid was isolated in the usual manner and crystallised thrice from dilute acetic acid in long, white needles, m.p. 71-72° (Bogert and Tuttle, *loc. cit.* give m.p. 71.7°).

(ii) *Keto-acids* (II, X).—2-Acetyl-*p*-cymene (10 g., 1 mol.) in dry ether (10 c.c., dry carbon tetrachloride is less favourable) was chilled in ice. A trace of anhydrous aluminium chloride was added and then bromine (3 c.c., 1 mol.) was added slowly in 1 c.c. portions, the second addition being made only when the first had been decolorised. Decolorisation was very rapid, though there was some initial lag. When the reaction was complete, ether and hydrogen bromide were removed immediately under suction in a very thin current of dry air. The syrupy liquid residue was then left in a vacuum desiccator overnight.

Sodium (1.27 g., 1 mol.) was powdered under 10 c.c. of dry xylene. The xylene was decanted off, the sodium washed with 10 c.c. portions of dry benzene twice and then immediately covered with dry benzene (20 c.c.). The appropriate malonic ester (1.1 mol.; diethyl malonate, 10.0 g.; methyl diethylmalonate, 10.5 g.) was added, the sodium salt was formed instantaneously appearing as a white gelatinous mass. When the initial reaction had subsided, the mixture was heated on the water-bath for 2 hours to complete the formation of the sodium salt and then cooled in ice.

The above ω -bromo-ketone was taken up in dry benzene (15 c.c.) and added all at once to the sodium salt of the malonic ester. The reaction started at room temperature; a lot of heat was generated, the complex began to dissolve with the precipitation of sodium bromide. When the reaction had slackened down (15 min.) the mixture was heated on the water-bath till all the sodium salt had dissolved (6 hours).

The reaction mixture was cooled, agitated with 50 c.c. of water and just acidified with dilute hydrochloric acid and then steam-distilled to remove the solvent and any unreacted malonic ester. The syrupy, reddish oil that remained was taken up in ether, the solution washed with water, dried over anhydrous sodium sulphate and evaporated. The residue was hydrolysed by refluxing for 5 hours with 15% alcoholic sodium hydroxide (100 c.c.). The reaction mixture was cooled, diluted with water, made just neutral with hydrochloric acid taking care that no acid precipitated out and then it was boiled with norit and filtered. The cooled solution was acidified with dilute hydrochloric acid, when the dibasic acid precipitated out as an oil which soon crystallised. The crystals were filtered off and heated in an oil-bath at 180-200° for half-an-hour to effect decarboxylation. The residue was crystallised from a suitable solvent.

β -(*p*-Cymoyl-2)-propionic acid (II) was obtained as colourless, prismatic needles (petrol ether 75°-90°), m.p. 76-77° and β -(*p*-cymoyl-2)- α -methylpropionic acid (X), as white plates (petrol ether & benzene, 2:1), m.p. 118-19°.

Syntheses of the Hydrocarbons

An Improved Method for the Preparation of Methylsuccinic Anhydride.—Several methods for the preparation of methylsuccinic acid are known (Higginbotham and Lapworth, *J. Chem. Soc.*, 1922, **121**, 51; "Organic Syntheses", XXVI, p. 54; Verkade and Hartman, *Rec. trav. chim.*, 1932, **52**, 947; Meyer and Stamm, *Ber.*, 1923, **56**, 1426;

Adkins and Wojcik, *J. Amer. Chem. Soc.*, 1934, **56**, 2424; Bischoff and Guthzeit, *Ber.*, 1881, **14**, 614; Bone and Sprankling, *J. Chem. Soc.*, 1899, **78**, 853). The following modification of Bone and Sprankling's method (*loc. cit.*) gave the best results.

Sodium (23 g., 1 atom) was powdered under xylene (150 c.c.) in a three-necked flask (2 litre) fitted with a stirrer (mercury sealed), a condenser carrying a guard tube and a dropping funnel. The xylene was decanted off and replaced by dry toluene (1 litre). The stirrer was started and ethyl malonate (1 mol., 160 g.) was added rapidly (15 min.). The reaction was rapid and when it had slowed down (half-an-hour), the mixture was refluxed with stirring for 3 hours and then cooled to room temperature. α -Bromopropionic ester (181 g., 1 mol.) was added dropwise to the rapidly stirred jelly of the sodium salt (2 hours). The reaction mixture was left overnight and then refluxed for 6 hours. The mixture was diluted with water, the toluene layer separated, washed with water, dilute hydrochloric acid (twice) and then with water. The wet toluene solution was distilled in vacuum to remove the toluene and the residual oily liquid was heated in an oil-bath at 170° under 100 to 120 mm. pressure to remove the unreacted components. The ester was next refluxed with 500 c.c. of concentrated hydrochloric acid till the oily layer had disappeared (7-10 hours). The mixture was then poured in an evaporating basin and the hydrochloric acid removed on the water-bath; the residue was cautiously treated with small amounts of concentrated nitric acid (twice) to oxidise the impurities and then evaporated with water till all the nitric acid had been expelled. The syrup was cooled to room temperature with stirring when it had solidified completely. Yield of the crude acid of m.p. 100-105° was 105 g. to 120 g. (80-90% of theory).

Acetyl chloride (150 c.c.) was added slowly to the crude acid (105 g.) placed in a flask carrying a reflux condenser with a guard tube. After the initial reaction had subsided, the mixture was refluxed for 2 hours on a water-bath and then fractionated in vacuum. The anhydride boiled at 118-120°/7 mm. as a colourless, oily liquid, yield 75 g. (83.3%). A small amount (0.2 g.) was evaporated to dryness with water (5 c.c.) to give pure methylsuccinic acid, m.p. 112°.

(i) *Condensation of Succinic and Methylsuccinic Anhydrides with p-Cymene: Formation of β -(p-Cymoyl-2)-propionic Acid (II) and β -(p-Cymoyl-2-) α -methylpropionic Acid (X).*—*p*-Cymene (purified by sulphuric acid treatment, 35 g., 41 c.c., 1.1 mol.), acid anhydride (1 mol., methylsuccinic anhydride, 28 g. or succinic anhydride, 24.4 g.) and freshly distilled nitrobenzene (150 c.c.) were placed in a 2-litre, three-necked flask carrying a mercury-sealed stirrer, a thermometer and an exit tube (CaCl₂ guard tube); the third neck was used for adding the anhydrous aluminium chloride. The mixture was stirred vigorously and cooled to -5° in a salt-ice mixture bath. Anhydrous aluminium chloride (74 g., 2.2 mol.) was added during 1½ hours in 4 lots; during these additions the temperature was not allowed to go beyond 10°. The stirring was then continued in the ice-bath for 3 hours more. The ice-bath was replenished, stirring stopped and the reaction mixture left overnight (12 hours). Next day the mixture was stirred for 2 hours at room temperature (22°). The reaction mixture had an appearance of a clear orange-red syrup which was transferred to a litre round-bottom flask, chilled in an ice-salt mixture and the complex decomposed with 200 g. of crushed ice followed by 60 c.c. of concentrated hydrochloric acid. The mixture was allowed to stand for an

hour and then steam-distilled to remove practically all the nitrobenzene. The residue was poured into a beaker (1 litre), cooled and some ice added; the oil soon solidified on slight scratching to a nearly white mass, which was filtered, washed with water and dissolved in aqueous sodium carbonate solution (water, 250 c.c., sodium carbonate, 40 g.). The solution was boiled to remove the last traces of nitrobenzene, treated with norit (if necessary) and filtered to remove some inorganic material. The filtrate and the washings were combined, cooled and acidified with hydrochloric acid (Congo red). The solid acid was removed by filtration, washed several times and then dried in a vacuum desiccator.

β-(p-Cymoyl-2-)-propionic Acid (II).—Yield of the crude product was 85%; it crystallised from petrol ether (75°–90°) in stout prisms and prismatic needles, m.p. 76–77°, yield 40 g. (70%). The product is very soluble in alcohol, benzene and ethyl acetate. It dissolves in concentrated sulphuric acid to give a deep yellow solution and melts to a red liquid. (Found: C, 71.13; H, 7.9. $C_{14}H_{18}O_3$ requires C, 71.79; H, 7.69 per cent).

β-(p-Cymoyl-2-)-α-methylpropionic Acid (X).—Yield of the crude product was 80.5%; it crystallised from 2 parts of a mixture of benzene (1 part) and petrol ether (75°–90°, 2 parts) in plates and prisms crystallising in stars, m.p. 118–19°, yield 36.5 g. (60%). (Found: C, 72.81; H, 8.34. $C_{15}H_{20}O_3$ requires C, 72.58; H, 8.06 per cent).

A longer time of reaction, or a higher temperature increased the yield of the crude product, but decreased that of the pure compound.

(ii) *Clemmensen's Reduction of (II) and (X): Formation of γ-(p-Cymyl-2-) butyric Acid (III) and γ-(p-Cymyl-2-)-α-methylbutyric Acid (XI).*—The pure acid (15 g.) was reduced with zinc amalgam (from 37 g. zinc wool, 3.7 g. of mercuric chloride, 2 c.c. of conc. hydrochloric acid and 55 c.c. of water) and hydrochloric acid (conc., 65 c.c. and water, 27 c.c.) with the addition of toluene (37 c.c.) and glacial acetic acid (2 c.c.) by refluxing for 34 hours in an oil-bath at 120°–140°. After every 6 hours, 15 c.c. of hydrochloric acid (conc.) were added. The reaction mixture was cooled, the toluene layer separated, washed with water and the wet solution distilled under reduced pressure to remove the toluene. The residue was distilled from a modified Claisen's flask in vacuum.

γ-(p-Cymyl-2-)-butyric Acid (III) was obtained as a thick colourless oil, b.p. 170–75°/3 mm., yield 12.5 g. (86%). Ruzicka (*Helv. Chim. Acta*, 1922, 5, 714) gives b.p. 195–200°/12 mm.

The small residue left after distilling (III) was boiled with water, cooled and the solid collected by filtration. On crystallisation from glacial acetic acid it formed small silky needles, m.p. 210–11°, yield 1 g.

γ-(p-Cymyl-2-)-α-methylbutyric Acid (XI) was obtained as a thick colourless liquid, b.p. 176–78°/3 mm., yield 11 to 13.5 g. (80–95.7%). Ruzicka (*Helv. Chim. Acta*, 1922, 5, 369) gives b.p. 200–201°/11 mm.

(iii) *Ring-closure of (III) and (XI): Formation of 5-Methyl-8-isopropyltetralone-1 (IV) and 2:5-Dimethyl-8-isopropyltetralone-1 (XII).*—Phosphorus pentachloride (9.8 g., 1.1 mol.) was placed in a distillation flask (100 c.c., side tube plugged) and covered with 15 c.c. of dry benzene. The acid (1 mol., 10 g.), dissolved in dry benzene (20 c.c.), was added in 2 lots to PCl_5 and the acid chloride was prepared in the usual manner. The benzene and the $POCl_3$ were removed by distillation under vacuum at a temperature not exceeding 90°; the discolorisation of the acid chloride was avoided.

Anhydrous aluminium chloride (6.2 g., 1.1 mol.) was placed in a 100 c.c. conical flask carrying a calcium chloride guard tube, and immediately covered with ligroin (free from unsaturation and aromatics, b.p. 75°-90°, 20 c.c.) and cooled in an ice-salt bath at -10°. The acid chloride was taken up in thiophen-free benzene (20 c.c.) and also cooled in an ice-bath. The thoroughly cooled acid chloride solution was added all at once to the aluminium chloride-ligroin mixture and swirled. On warming to room temperature (24°) the reaction started with vigorous evolution of hydrochloric acid gas. The reaction with the chloride of (*p*-cymyl-2-)-butyric acid (III) was more rapid and started at a lower temperature. When the vigour of the reaction had subsided, the mixture was just warmed on a water-bath at 50° and taken out, and the reaction allowed to proceed as such; this was repeated (3-4 times) till all the aluminium chloride had just disappeared. The mixture was dark black in colour. This was poured on to ice (100 g.) and hydrochloric acid (conc., 15 c.c.) and kept for half-an-hour with occasional stirring. Ether (about 25 c.c.) was added and the red solvent layer removed, washed successively with dilute hydrochloric acid, water, dilute caustic soda (twice) and water, and dried over anhydrous sodium sulphate. The residue, left after removal of the solvents under diminished pressure, was distilled from a 20 c.c. modified Claisen's flask.

5-Methyl-8-isopropyltetralone (IV) was obtained as a colourless, mobile oil, b.p. 163°-66°/11 mm., yield 70%. 2:4-Dinitrophenylhydrazone (sulphuric acid method) gave bright red, flat needles (benzene & petrol), m.p. 198.5-199.5°. (Found: N, 14.51. $C_{20}H_{22}O_4N_4$ requires N, 14.65 per cent).

2:5-Dimethyl-8-isopropyltetralone (XII) was obtained as a colourless, very slightly viscous liquid, b.p. 141-42°/3 mm., yield 8.0 g. (87%). The liquid crystallised out completely after a day as stout, large prisms (petrol ether, 40°-60°), m.p. 50-51°. (Found: C, 82.46; H, 9.87. $C_{18}H_{20}O$ requires C, 83.33; H, 10.18 per cent). 2:4-Dinitrophenylhydrazone, prepared as above, gave bright red, lustrous, needle-like plates, crystallising in stars (petrol & benzene), m.p. 212.5-213.5°. (Found: N, 14.09. $C_{21}H_{24}O_4N_4$ requires N, 14.14 per cent).

(iv) 1-Methyl-4-isopropyl*naphthalene* (apo-Cadalene) (VI).—The ketone (IV, 6 g.), dissolved in absolute alcohol (60 c.c.), was reduced in the usual manner with sodium (4 g.).

The crude reduction product (5.7 g.) was dehydrogenated by heating with selenium (4 g.) in a metal-bath at 180°-200° for 1 hour till all the dehydration water had been expelled, and then heating at 260°-280° for 17 hours, when the evolution of hydrogen selenide had ceased completely. The cooled reaction mixture was extracted with ether, the ether evaporated and the residual oil distilled over sodium in vacuum, when 5 g. of a colourless mobile oil, b.p. 162°-175°/18 mm. were obtained. The hydrocarbon was purified by regeneration from the picrate and then had b.p. 145-48°/11 mm. *Picrate*, orange needles from alcohol, m.p. 99-100° Ruzicka and Migazzini (*loc. cit.*) gives m.p. 99-100°.

(v) *Cadalene* (XIV).—The crystalline ketone (XII, 4.5 g.) in benzene (40 c.c.) was placed in a three-necked flask carrying a reflux condenser, a dropping funnel and a mercury-sealed stirrer. Sodium (8 g., cut in very thin slices) was added to the

benzene solution and 20 c.c. of water were added at a very slow rate to the rapidly stirred solution, till all the sodium had reacted ($1\frac{1}{2}$ hours). The reaction mixture was diluted with water, the benzene layer removed and washed with dilute hydrochloric acid and then twice with water. The wet solution was distilled to remove the benzene, the last traces being removed in vacuum, when 4 g. of a slightly coloured, mobile liquid were left. The crude carbinol was dehydrated with 90% formic acid (6 g.) for 2 hours at 80° , and the unsaturated hydrocarbon isolated in the usual manner as a colourless, mobile liquid, b.p. 132° - $140^\circ/9$ mm., yield 2.8 g. (73%). The compound was unsaturated to bromine in chloroform.

To the dihydrocadalene (2.8 g.) selenium (3 g.) was added and the mixture heated first at 280° - 290° for 10 hours and finally at 310° - 320° for 15 hours, when no more hydrogen selenide was evolved. The cadalene was isolated with ether in the usual manner and distilled over sodium, b.p. 132 - $140^\circ/4.5$ mm., yield 1.5 g. (55%). *Picrate*: orange-yellow needle (alcohol), m.p. 115 - 16° , mixed m.p. with an authentic sample (natural source) remained undepressed. Ruzicka (*loc. cit.*) gives m.p. 114 - 15° .

ORGANIC CHEMISTRY LABORATORIES,
DEPT. OF PURE & APPLIED CHEMISTRY,
INDIAN INSTITUTE OF SCIENCE, BANGALORE.

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STUDIES ON YEAST NUCLEIC ACID. PART II. INTERACTION WITH BASES AND ACIDS

By S. N. MUKHERJEE AND NIRMAL KUMAR SARKAR

Interaction of the yeast nucleic acid with bases and acid has been studied by potentiometric and conductometric titrations. Results of potentiometric titration with $\text{Ba}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, KOH , NaOH and NH_4OH show that this nucleic acid has no fixed total acidity which is found to vary slightly in the order: $\text{Ba}(\text{OH})_2 > \text{Ca}(\text{OH})_2 > \text{KOH} > \text{NaOH} > \text{NH}_4\text{OH}$. Conductometric titration curves with $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ present peculiar shapes. Nucleic acid interacts with HCl in the same way as phosphoric acid.

From variation of H-ion activity, specific conductance and cataphoretic velocity with concentration of the yeast nucleic acid solution as communicated in Part I of this series (*J. Indian Chem. Soc.*, 1947, **24**, 65) it was concluded that there might be some type of aggregate formation on the part of the anions (nucleate ions) occurring in this system. It has also been observed that there is no definite critical concentration for these systems because different physical properties, when plotted against concentration of the solution, show breaks in different concentration regions, widely differing from one another. Thus, the nature of variation of the physical properties together with the absence of any definite critical concentration (*cf.* Hartley, *Kolloid Z.*, 1939, **88**, 22) has led to the conclusion that most probably in these systems the process of aggregate formation is not sudden but progressive, proceeding at all concentrations and different physical and electrochemical properties, when plotted against concentration, show breaks depending on the nature of the property and the degree of aggregation.

The present investigations were undertaken with a view to examining this point further from evidences obtained from interaction of the yeast nucleic acid solution with different bases and acids.

Both potentiometric and conductometric methods have been employed. Five different bases viz., NH_4OH , NaOH , KOH , $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ have been studied in this connection. The acid used was HCl only.

EXPERIMENTAL

The methods of purification of the acid and preparation of the sol were the same as reported in Part I (*loc. cit.*). The acid content of these solutions was approximately the same viz., 2 g. per litre of the solution.

Potentiometric and conductometric measurements were carried out at $35 \pm 0.1^\circ$ in an electrically regulated thermostat. Usual precautions, *e.g.*, frequent replatinisation of the platinised platinum electrodes, were taken for p_H measurements (*vide* J. N. Mukherjee, and co-workers, *J. Indian Agric. Sci.*, 1936, **6**, 571). Quinhydrone electrode has not been used in these titrations as this is known to yield inaccurate results beyond p_H 7.6.

Interaction with Bases

(i) *Potentiometric Titration.*—Reproducibility of the potentiometric measurements was first checked by titrating the same solution on two different occasions by the same base, *e.g.*, NaOH . The result is presented in Fig. 1. The two titration curves run

almost coincident, so much so, that it is difficult to distinguish them as two distinct curves for the greater part of their course.

From titration curves with different bases, given in Fig. 2, it is evident that with all the bases excepting NH_4OH the titrations could be pushed to a high p_H (above 10). With NH_4OH , the titration curve becomes flat beyond p_H 5.8 (approx.) above which the slope of the curve is found to diminish appreciably probably because NH_4OH is driven off from the solution as NH_3 by bubbling of hydrogen gas, before it could react with the acid.

FIG. 1

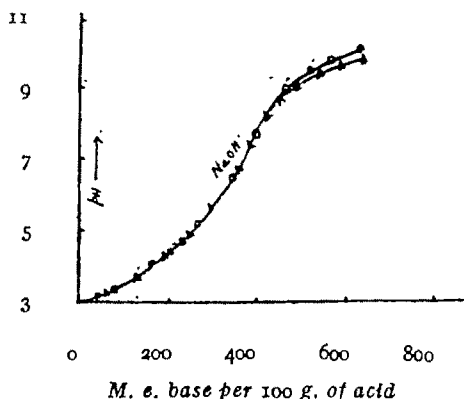
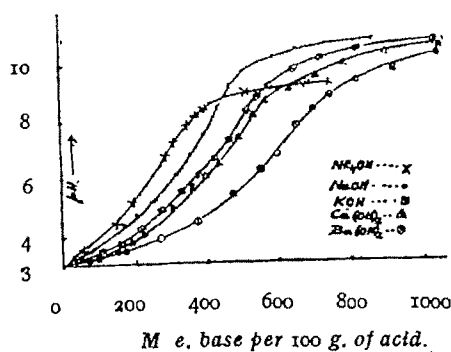


FIG. 2



Titration curves as evident from the figure, never shoot up sharply in any region but lie flat with a relatively steep slope in a certain region indicative of an inflexion. The inflexion, occurring in each case between p_H 5 and 8, is nowhere very steep. The curves have all a comparatively flat initial portion followed by inflexions and final flattening at higher p_H values. The slow rise of the curve beyond the steeper inflexion indicates a continued interaction with the base even in this region. This portion occurs in almost all cases between p_H 10 and 11 excepting with NH_4OH , as already mentioned.

The titration curves with the different bases are not coincident. The curve for $\text{Ba}(\text{OH})_2$ shows a longer flat portion in the initial stages of titration indicative of a relatively high buffering in this region. The titration curve for NH_4OH shows a steeper rise almost from the beginning. The initial buffering of the $\text{Ba}(\text{OH})_2$ curve may be either due to the relative insolubility of the barium salt of the nucleic acid or to the higher coagulating power of the Ba -ion for this solution. Further, it may be mentioned that the courses of the titration curves are not such as to warrant the polybasicity of the acid from a casual inspection. This evidently suggests that either the acid is monobasic or, if polybasic, its dissociation constants are so close to one another as not to exhibit separate inflexions in the titration curves, *i.e.*, the inflexions overlap and present the characteristics of one continuous inflexion (Steudel, *Z. physiol. Chem.*, 1921, 18, 119; Simms, *J. Amer. Chem. Soc.*, 1926, 48, 1239, 1251).

To clarify this point it was thought desirable to analyse the titration curves further by drawing their buffer capacity curves (Van Slyke, *J. Biol. Chem.*, 1922, 22, 525) by plotting db/dp_H against mean base, presented for one typical base in Fig. 3A. The buffer capacity curves are evidently complex and the existence of more than one minimum

is not clearly discernible. It was therefore necessary to try other methods for deciding this point unequivocally. The acid was therefore titrated by diluted bases very carefully (instead of using approximately ten times stronger bases). The two titration curves presented in Fig. 3B for NaOH and Ba(OH)₂ bring out clearly the existence of two in-

FIG. 3A

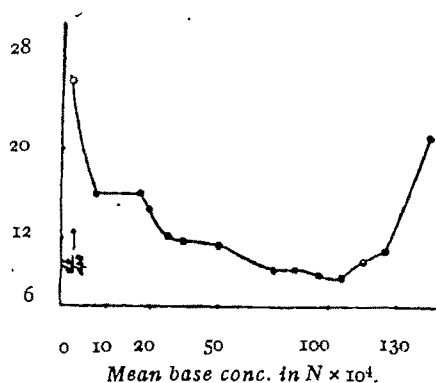
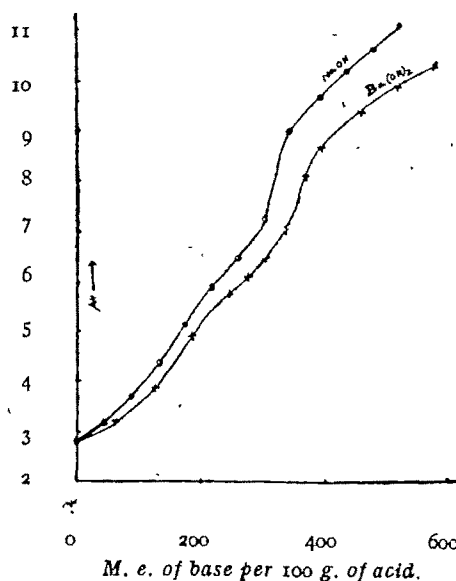


FIG. 3B



flexion points in the whole run of the curve up to p_H 10. All the other bases were similarly tried and in each case two inflexion points were visually noticeable. Titration curves of NaOH and Ba(OH)₂ have only been presented here and the rest not shown for economy of space. A summary of the analysis of these curves is presented in Table I below.

TABLE I

Base.	First inflexion		Second inflexion	
	p_H .	M.e. base per 100 g. acid.	p_H .	M.e. base per 100 g. acid
NH ₄ OH	4.90	150	7.00	310
NaOH	4.75	165	7.10	325
KOH	4.60	168	7.00	360
Ca(OH) ₂	4.50	172	7.10	382
Ba(OH) ₂	4.30	182	7.10	390

It is evident from the above table that the p_H of the first inflexion with all the bases lies in the neighbourhood of 4.5 to 4.9, with about 165 m.e. of base per 100 g. of the acid. The concentration of the solution was 2 g. per litre and hence the actual amount of base required for this inflexion amounted to $2 \times 165 / 100 \times 10^{-3} = 3.3 \times 10^{-3}$ equivalents. The initial p_H of the acid solution was 2.95, whence $a_H = 1.2 \times 10^{-3}$. Hence the base required at the first inflexion is greater than that required to neutralise free acidity (hydrogen-ion activity).

The base required for the second inflexion-point, which is the sharper of the two, gives the total acidity per 100 g. of the nucleic acid, since no further inflexion point

could be detected beyond this point up to p_H 10. Obviously the total acidity is not exactly a fixed quantity with the different bases studied but shows a slight variation in the order : $Ba(OH)_2 > Ca(OH)_2 > KOH > NaOH > NH_4OH$. Total acidity at a definite p_H also runs in the same order. The difference observed with different bases is, however, not very marked.

Calculating from the total acidity observed with NaOH viz., 325 m.e. per 100 g. of the acid, the equivalent weight of the acid roughly comes out to 308. Assuming the acid to be tetrabasic (cf. Steudel, *loc. cit.*) its molecular weight amounts to 1232. This compares favourably with the value of 1287 calculated from the simplest structural formula on the assumption of the tetranucleotidic composition of the acid.

Potentiometric titration curves thus show two dissociation constants and present the character of a weak acid. The ratio of free acidity per 100 g. of the acid, calculated from hydrogen-ion activity of the solution (viz., 1.2×10^{-3}), to the total acidity calculated for the same amount of the acid is 0.143 i.e., 14.3% only. Such low values can be expected of weak acids alone. The p_H of the second inflexion lies at about 7.1, a fact which is characteristic of strong acids alone. Such conflicting features cannot, however, be expected of acids in true solutions.*

(ii) *Conductometric Titration.*—Conductometric titrations were carried out with three different bases : KOH, $Ca(OH)_2$ and $Ba(OH)_2$. The results are graphically represented in Fig. 4. The curve for KOH shows two inflexions, one (A) corresponding to about 175 m.e. of base per 100 g. of the acid which tallies excellently with the first inflexion of the potentiometric titration curve. The second inflexion (B) occurs at about 370 m.e. of base which is also almost equal to the total acidity for 100 g. of the acid obtained potentiometrically. The course of the curve beyond second inflexion simulates strongly the alkali line. Between these two inflexions the specific conductance of the sol rises with addition of base to a value much above that for the original sol, and the curve thus resembles that of a weak acid.

FIG. 4

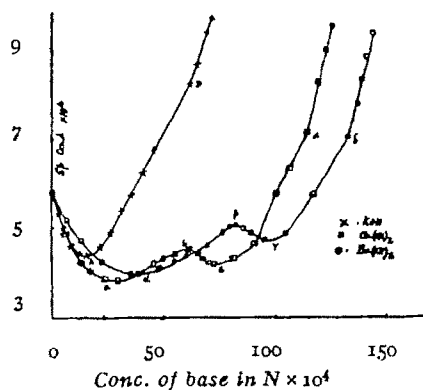
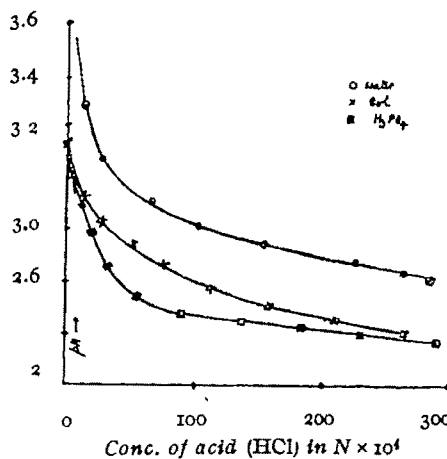


FIG. 5



* Reference may be made in this connection to the extensive work on the potentiometric titration of different colloidal acids carried out by Prof. J. N. Mukherjee and co-workers published in this journal and also in *Indian J. Agric. Sci.*

Titration curves with $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ present a complex character. First inflexion points (a and a') for these bases exhibit slight difference from each other and they are both higher than that for KOH. The curves for $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ are W-shaped. The final inflexion points (d and d') are far removed from those obtained by potentiometric titration with these bases. From the shape of the curves the relative order of total acidity appears to be the same as observed from potentiometric study viz., $\text{Ba}(\text{OH})_2 > \text{Ca}(\text{OH})_2 > \text{KOH}$.

The peculiar shapes of the conductometric titration curves with $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ are, however, difficult of explanation at the present stage. Further work appears to be necessary to get an insight into the mechanism going on in the system during its interaction with these bases. It is quite likely that the divalent cations, Ba^{++} and Ca^{++} , besides neutralising the acid, have in addition a precipitating effect either due to the formation of insoluble salts or by coagulation on the colloidal micelles of the nucleic acid anions. This point will form the subject matter of a future communication.

Interaction with Acid

A preliminary investigation was carried out by titrating a nucleic acid solution with HCl in the same way as in the case of the bases mentioned above. The hydrochloric acid solution used was approximately 10 times as strong as the nucleic acid solution in order to avoid any dilution effect when HCl was mixed with nucleic acid solution. Results have been graphically presented in Fig. 5.

For comparison, a study of the interaction of water with hydrochloric acid solution and of phosphoric acid with hydrochloric acid solution was also conducted in the same manner as with the nucleic acid solution. Results are shown graphically in the same figure. The phosphoric acid solution used was of the same p_H as the nucleic acid solution.

It will be evident from the figure that the curve for the nucleic acid occupies an intermediate position between those for water and phosphoric acid solutions. Nucleic acid solution has a greater buffering action compared to phosphoric acid since the p_H for equal additions of HCl is much higher with nucleic acid than with the latter.

It is well known that acidic properties of nucleic acids owe their origin to the existence of ionisable phosphoric acid groups present in the molecule. Hence a close similarity was expected in the interaction of nucleic and phosphoric acids with HCl. Although a broad similarity does actually exist, the difference at the same time is quite marked.

Levene ("Nucleic Acids", 1931, p. 284), however, concludes from the structure proposed by him that the phosphoric acid groups in the nucleic acid have only one ionisable hydrogen atom left for ionisation excepting one group which possesses two such atoms. Hence, the phosphoric acid groups should exhibit the primary dissociation mainly excepting one group which should show a secondary dissociation as well. In the phosphoric acid itself all the three different types of dissociation are probable and possibly they do exist. In the light of these observations it is quite rational to expect some difference between the two acids although both of them contain phosphoric acid groups responsible for its electrolytic ionisation. But whether this is quite sufficient to explain the observed facts awaits further investigation.

C O N C L U S I O N S

1. Potentiometric titrations of yeast nucleic acid were carried out with five different bases viz., NH_4OH , NaOH , KOH , $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$. Titration curves do not show very sharp inflexions characteristic of strong or moderately strong acids.

2. Further analysis of these curves brings out only two definite inflexions, the first one being slightly greater than that corresponding to the neutralisation of the free acidity. The p_H 's of the two inflexions are more or less the same for the different bases, the first one showing a greater variation (from 4.9 to 4.3) while the second one being more steady at 7.0 to 7.1, as the interacting base is changed.

3. The nucleic acid has no definite total acidity which has been observed to vary with the nature of the base used for interaction. The differences are, however, small and run in the order: $\text{Ba}(\text{OH})_2 > \text{Ca}(\text{OH})_2 > \text{KOH} > \text{NaOH} > \text{NH}_4\text{OH}$.

4. Conductometric titrations with $\text{Ba}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ and KOH also exhibit similar behaviour. KOH shows two inflexions and they fairly correspond with those of the potentiometric titration within limits of experimental accuracy. The titration curves for $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ present peculiar shapes. Total acidities show the same order of variation as in potentiometric titration with which they roughly agree.

5. Nucleic acid interacts with HCl in the same way as water and phosphoric acid. The difference is more quantitative than qualitative in nature.

PHYSICAL CHEMISTRY LABORATORIES,
COLLEGE OF ENGINEERING & TECHNOLOGY, JADAVPUR,
AND
UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY,
CALCUTTA.

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PHYSICO-CHEMICAL STUDIES ON THE COMPOSITION OF COMPLEX
FERRO AND FERRICYANIDES. PART III. CONDUCTOMETRIC
STUDIES ON THE COMPOSITION OF COPPER
FERROCYANIDE

By ABANI K. BHATTACHARYA AND HARISH C. GAUR

The composition of copper ferrocyanide has been studied by the conductometric titration of copper sulphate and potassium ferrocyanide and the results discussed in relation to the conclusions derived from thermometric and potentiometric titrations (Parts I and II).

In previous parts of this series (*this Journal*, 1947, **24**, 487, 499) the composition of copper ferrocyanide has been studied by thermometric and potentiometric methods of titrations. In this paper the composition has been studied by the conductometric titrations of copper sulphate and potassium ferrocyanide. The conductometric results have been discussed *vis a vis* the conclusions derived from thermometric and potentiometric titrations.

EXPERIMENTAL

'Analar' (B.D.H.) reagents were used. Preparation of standard solutions and all further dilutions were made with conductivity water. The conductivities were measured by Kohlrausch's Universal Bridge (W. G. Pye Ltd.) As a source of alternating current a small induction coil was used, the point of balance being indicated by the minima of sound in the telephone. The cell used was of Arrhenius type and was immersed in a thermostat whose temperature was controlled within $\pm 0.1^\circ$. For carrying the titrations 10 c.c. of one of the reagents were taken in the conductivity cell, while the other was added from the burette. The conductance of the solution after each addition was measured. This was carried on till about 1 to 2 c.c. of the titrating liquid was added in excess of the equivalence point, which could be easily known from the increase or decrease in the conductivities observed. The conductance obtained after each addition was corrected for dilution by multiplying the observed conductance by $V/10$, where 'V' is the total volume of the solution, and 10 c.c. refer to the volume of the reactant originally taken in the cell (Davies, "The Conductivity of Solutions", p. 238). Curves were plotted between the corrected conductance so obtained against the volume of the titrant. The equivalence point was obtained as a point of intersection of the two portions of the curve. In the case where the two portions were joined by a curve of inflection, the middle point of inflection was taken as the equivalence point.

Using different concentrations of the two salt solutions, titrations were followed by the direct and reverse methods of titrations (*i.e.*, when copper sulphate from burette was added to potassium ferrocyanide taken in the cell and *vice versa*). Titrations were also done in the presence of alcohol up to a total concentration of 20% by volume. $M/5$ solution of copper sulphate would be referred as A/1 solution and $M/4.94$ solution of potassium ferrocyanide solution, as A/1 solution of K_4FeCy_6 .

Direct Conductometric Titrations

Copper sulphate from the burette was added to potassium ferrocyanide in the cell, and mixed with varying amounts of alcohol.

TABLE I

Vol. of A/10-K₄FeCy₆=10 c.c. Alcohol=nil. (Fig. 1, curve 1).

A/1-CuSO ₄ added.	Total vol.	Cor. condy. (mho)	A/1-CuSO ₄ added.	Total vol.	Cor. condy. (mho)	A/1-CuSO ₄ added.	Total vol.	Cor. condy. (mho)
0.0 c.c.	10.0 c.c.	23.26×10^{-3}	0.8 c.c.	10.8 c.c.	20.50×10^{-3}	1.3 c.c.	11.3 c.c.	19.41×10^{-3}
0.2	10.2	22.66	1.0	11.0	19.82	1.4	11.4	19.83
0.4	10.4	21.89	1.1	11.1	19.38	1.5	11.5	20.84
0.6	10.6	21.20	1.2	11.2	19.31	1.6	11.6	21.81
						1.7	11.7	22.63

TABLE II

A/10-K₄FeCy₆ soln.=9 c.c. Alcohol=1 c.c. (Fig. 2, curve 2).

A/1-CuSO ₄ added.	Total vol.	Cor. condy. (mho.)	A/1 CuSO ₄ added.	Total vol.	Cor. condy. (mho)
0.0 c.c.	10.0 c.c.	15.04×10^{-3}	1.1 c.c.	11.1 c.c.	13.62×10^{-3}
0.4	10.4	14.82	1.2	11.2	13.75
0.6	10.6	14.42	1.3	11.3	14.31
0.8	10.8	14.04	1.4	11.4	15.20
1.0	11.0	13.72	1.7	11.7	16.84

TABLE III

A/10-K₄FeCy₆ soln.=8 c.c. Alcohol=2 c.c. (Fig. 2, curve 3).

A/1-CuSO ₄ added.	Total vol.	Cor. condy. (mho)	A/1-CuSO ₄ added.	Total vol.	Cor. condy. (mho)	A/1-CuSO ₄ added.	Total vol.	Cor. condy. (mho)
0.0 c.c.	10.0 c.c.	95.24×10^{-4}	0.6 c.c.	10.6 c.c.	94.2×10^{-4}	1.1 c.c.	11.1 c.c.	96.11×10^{-4}
0.2	10.2	96.68	0.7	10.7	93.45	1.2	11.2	101.4
0.4	10.4	95.82	0.9	10.9	92.76	1.5	11.5	115.6
0.5	10.5	95.06	1.0	11.0	92.81	1.6	11.6	119.0

TABLE IV

Vol. of A/10-K₄FeCy₆=10 c.c. Alcohol=nil. (Fig. 3, curve 4).

A/2-CuSO ₄ added.	Total vol.	Cor. condy. (mho)	A/2-CuSO ₄ added.	Total vol.	Cor. condy. (mho)	A/2-CuSO ₄ added.	Total vol.	Cor. condy. (mho)
0.0 c.c.	10.0 c.c.	23.53×10^{-3}	1.6 c.c.	11.6 c.c.	21.40×10^{-3}	2.8 c.c.	12.8 c.c.	21.16×10^{-3}
0.4	10.4	23.01	2.2	12.2	20.62	3.0	13.0	21.85
0.8	10.8	22.50	2.4	12.4	20.34	3.2	13.2	22.56
1.2	11.2	21.93	2.6	12.6	20.39	3.4	13.4	23.32

TABLE V

Vol. of A/10-K₄FeCy₆=9 c.c. Alcohol=1 c.c. (Fig. 4, curve 5).

A/2-CuSO ₄ added.	Total vol.	Cor. condy. (mho)	A/2-CuSO ₄ added.	Total vol.	Cor. condy. (mho)	A/2-CuSO ₄ added.	Total vol.	Cor. condy. (mho)
0.0 c.c.	10.0 c.c.	15.15 × 10 ⁻³	1.8 c.c.	11.8 c.c.	14.48 × 10 ⁻³	2.6 c.c.	12.6 c.c.	15.81 × 10 ⁻³
0.4	10.4	15.18	2.0	12.0	14.28	2.8	12.8	16.00
0.8	10.8	15.01	2.2	12.2	14.27	3.0	13.0	16.90
1.2	11.2	14.84	2.4	12.4	14.51	3.2	13.2	17.49

TABLE VI

Vol. of A/10-K₄FeCy₆=8 c.c. Alcohol=2 c.c. (Fig. 4, curve 6).

A/2-CuSO ₄ added.	Total vol.	Cor. condy. (mho)	A/2-CuSO ₄ added.	Total vol.	Cor. condy. (mho)	A/2-CuSO ₄ added.	Total vol.	Cor. condy. (mho)
0.4 c.c.	10.4 c.c.	10.15 × 10 ⁻³	1.8 c.c.	11.8 c.c.	10.00 × 10 ⁻³	2.4 c.c.	12.4 c.c.	11.07 × 10 ⁻³
0.8	10.8	10.09	2.0	12.0	10.08	2.6	12.6	11.89
1.2	11.2	10.05	2.1	12.1	10.25	2.8	12.8	12.59
1.6	11.6	10.00	2.2	12.2	10.47	3.0	13.0	12.94

Reverse Conductometric Titrations

K₄Fe(CN)₆ solution from the burette was added to CuSO₄ solution in the cell and mixed with varying amounts of alcohol.

TABLE VII

Vol. of A/10-CuSO₄=10 c.c. Alcohol=nil. (Fig. 5, curve 7).

A/2-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)	A/2-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)	A/2-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)
0.0 c.c.	10.0 c.c.	8.33 × 10 ⁻⁴	0.8 c.c.	10.8 c.c.	12.83 × 10 ⁻⁴	1.3 c.c.	11.3 c.c.	15.44 × 10 ⁻⁴
0.2	10.2	9.31	1.0	11.0	14.10	1.4	11.4	16.01
0.4	10.4	10.50	1.1	11.1	14.80	1.6	11.6	17.80
0.6	10.6	11.72	1.2	11.2	15.12	1.8	11.8	19.77

TABLE VIII

Vol. of A/10-CuSO₄=9 c.c. Alcohol=1 c.c. (Fig. 5, curve 8).

A/2-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)	A/2-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)	A/2-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)
0.0 c.c.	10.0 c.c.	62.11 × 10 ⁻⁴	0.8 c.c.	10.8 c.c.	100.9 × 10 ⁻⁴	1.3 c.c.	11.3 c.c.	118.7 × 10 ⁻⁴
0.2	10.2	68.00	1.0	11.0	109.5	1.4	11.4	125.3
0.4	10.4	78.52	1.1	11.1	111.0	1.6	11.6	139.0
0.6	10.6	89.07	1.2	11.2	114.0	1.8	11.8	155.3

TABLE IX

Vol. of A/10-CuSO₄=8 c.c. Alcohol=2 c.c. (Fig. 5, curve 9).

A/2-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)	A/2-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)	A/2-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)
0.0 c.c.	10.0 c.c.	31.75 × 10 ⁻⁴	0.6 c.c.	10.6 c.c.	59.55 × 10 ⁻⁴	1.2 c.c.	11.2 c.c.	84.22 × 10 ⁻⁴
0.2	10.2	40.00	0.8	10.8	70.59	1.4	11.4	97.01
0.4	10.4	49.06	1.0	11.0	76.67	1.6	11.6	111.0
			1.1	11.1	79.55	1.7	11.7	117.0

TABLE X

Vol. of A/10-CuSO₄=10 c.c. Alcohol=nil. (Fig. 6, curve 10).

A/4 K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)	A/4-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)	A/4-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)
0.0 c.c.	10.0 c.c.	78.13 × 10 ⁻⁴	2.0 c.c.	12.0 c.c.	141.7 × 10 ⁻⁴	2.7 c.c.	12.7 c.c.	158.4 × 10 ⁻⁴
0.4	10.4	88.50	2.2	12.2	147.9	2.8	12.8	162.7
0.8	10.8	100.9	2.4	12.4	150.3	2.9	12.9	168.6
1.2	11.2	113.7	2.6	12.6	154.6	3.2	13.2	183.5
1.6	11.6	126.4				3.6	13.6	206.0

TABLE XI

Vol. of A/10-CuSO₄=9 c.c. Alcohol=1 c.c. (Fig. 6, curve 11).

A/4-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)	A/4-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)	A/4-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)
0.0 c.c.	10.0 c.c.	49.50 × 10 ⁻⁴	2.0 c.c.	12.0 c.c.	110.1 × 10 ⁻⁴	2.4 c.c.	12.4 c.c.	117.0 × 10 ⁻⁴
0.4	10.4	60.11	2.1	12.1	111.0	2.6	12.6	124.2
0.8	10.8	71.53	2.2	12.2	112.4	2.8	12.8	133.1
1.2	11.2	83.55	2.3	12.3	114.4	3.2	13.2	152.6
1.6	11.6	97.90				3.4	13.4	160.5

TABLE XII

Vol. of A/10-CuSO₄=8 c.c. Alcohol=2 c.c. (Fig. 6, curve 12).

A/4-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)	A/4-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)	A/4-K ₄ FeCy ₆ added.	Total vol.	Cor. condy. (mho)
0.0 c.c.	10.0 c.c.	31.75 × 10 ⁻⁴	1.6 c.c.	11.6 c.c.	74.82 × 10 ⁻⁴	2.4 c.c.	12.4 c.c.	92.54 × 10 ⁻⁴
0.4	10.4	40.79	1.8	11.8	79.77	2.8	12.8	107.5
0.8	10.8	50.94	2.0	12.0	82.46	3.2	13.2	122.8
1.2	11.2	62.57	2.1	12.1	84.02	3.4	13.4	131.3
			2.2	12.2	85.90			

The variations in the titre values in presence of alcohol support the hydrolytic behaviour of copper ferrocyanide.

DISCUSSION

Considering the strengths of the solutions of copper sulphate (*M*/4.8) and potassium ferrocyanide (*M*/5.0), the theoretical titre values for 10 c.c. of K₄FeCy₆ for the formation of the compounds K₂CuFeCy₆, Cu₂FeCy₆ and K₂Cu₃(FeCy₆)₂ in direct titration would be 9.6, 19.2 and 14.4 c.c. respectively of copper sulphate solution. Theoretical titre values for the formation of the above compounds in the reverse titrations would be 10.42, 5.21 and 6.95 respectively of ferrocyanide solution.

In view of the hydrolysable character of the compound, the titre values in the aqueous medium in the case of direct titrations should be higher than the theoretical one. Compound K₂CuFeCy₆ would require 9.6 c.c. of CuSO₄ for 10 c.c. of K₄FeCy₆. But in the case of direct titrations the compound K₂Cu₃(FeCy₆)₂ is also likely to be formed, as has actually been observed in the thermometric and potentiometric studies. The observed titre values 12.8 to 13.54 in aqueous medium in the direct titrations therefore suggest that a mixture of K₂CuFeCy₆ and K₂Cu₃(FeCy₆)₂ is formed, and the average molecular proportion on the basis of conductometric results, comes to 1 : 3. The

FIG. 1

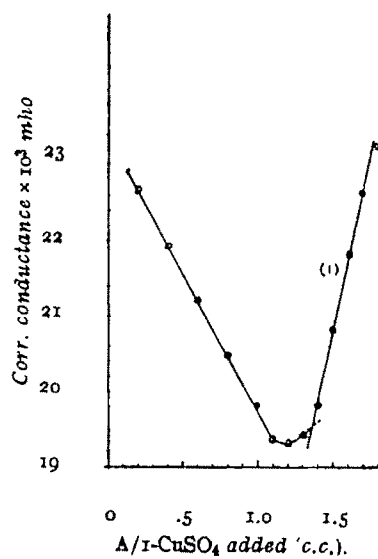


FIG. 3

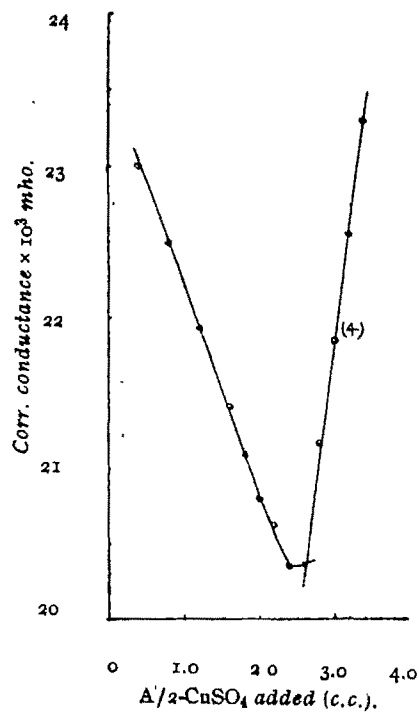


FIG. 2

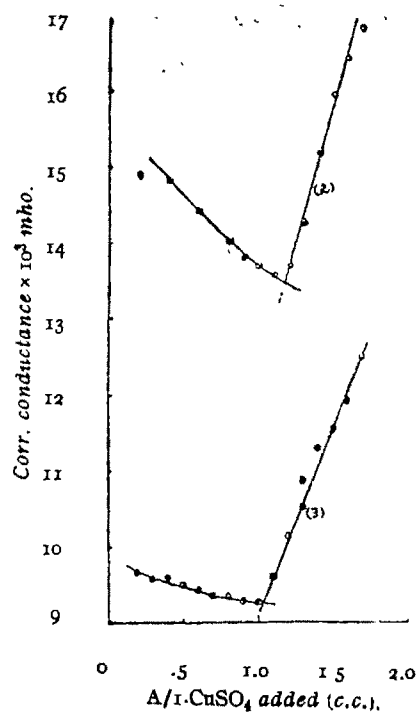
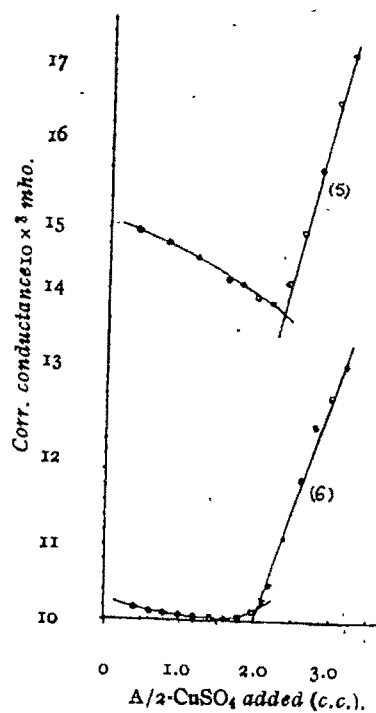


FIG. 4



decrease in the titre value in the presence of alcohol is explained as being due to the suppression of hydrolysis of the mixed compound formed.

FIG. 5

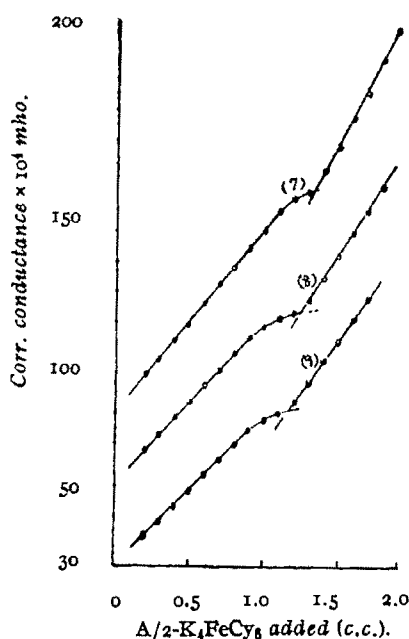
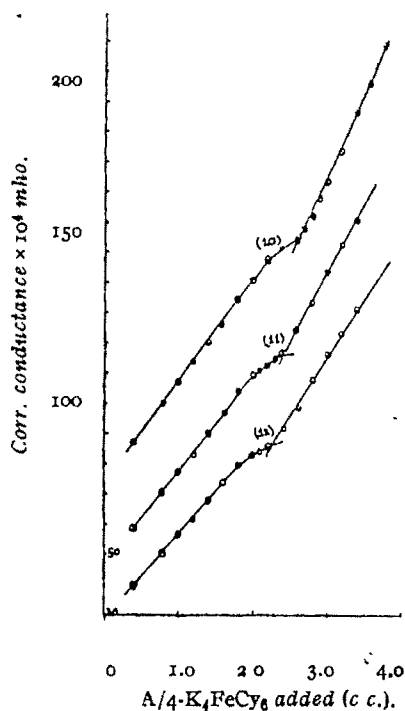


FIG. 6



In the reverse titrations the observed titre value 6.6 to 6.7 c.c. in aqueous medium is slightly lower than the theoretical one (6.9 c.c.) required for the formation of $K_2Cu_3(FeCy_6)_2$. In the presence of alcohol there is a gradual increase of the observed titre values which very nearly approach the theoretical one. These results again support the hydrolytic behaviour of copper ferrocyanide and the formation of $K_2Cu_3(FeCy_6)_2$ when the compound is precipitated in excess of $CuSO_4$.

Along with hydrolysis, adsorption of Cu^{++} and $Fe(CN)^{4-}$ ions also affects the composition of copper ferrocyanide, but the role of adsorption may be apparently suppressed and may not be accounted for by the titre values in consequence of the hydrolytic behaviour of such compounds. Quantitative estimations of the adsorption of Cu^{++} and $Fe(CN)^{4-}$ ions are in progress.

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CHEMICAL LABORATORIES,
AGRA COLLEGE, AGRA.

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VARIATION OF ABSOLUTE VISCOSITY WITH CONCENTRATION. ORGANIC SOLUTE IN NON-AQUEOUS SOLVENT

BY A. N. BOSE

The viscosity of non-electrolytes in non-aqueous solvent has been studied at different concentrations. It has been shown that Taimini's second equation, $\ln \eta = \theta c + \phi$ is more applicable to these systems than the first equation, $\eta = mc + n$. The values of the constants, θ and ϕ , of the second equation have been calculated.

A number of equations relating viscosity with concentration has been proposed from time to time. Out of these expressions the equation of Arrhenius

$$\frac{\eta_s}{\eta_o} = A^c \text{ or } \ln \frac{\eta_s}{\eta_o} = c \ln A \text{ or } kc$$

has been found to be most useful. This equation has been studied by Rehner (*Z. physikal. Chem.*, 1882, **2**, 744), Wagner (*ibid.*, 1891, **5**, 31) and others. They found that the equation was applicable within 1% up to 1N solutions in a number of cases. But Taimini and others have shown that the equation of Arrhenius is not applicable to the more concentrated solutions. Taimini (*J. Phys. Chem.*, 1928, **32**, 604; 1929, **33**, 56) proposed two equations

$$\eta = mc + n \quad \dots (1)$$

$$\ln \eta = \theta c + \phi \quad \dots (2)$$

He has applied these to the supersaturated solutions investigated by him. The second equation of Taimini can be shown to be equivalent to the equation of Arrhenius as given below :

$$\ln \frac{\eta_s}{\eta_o} = kc$$

$$\text{or } \ln \eta_s - \ln \eta_o = kc$$

$$\text{or } \ln \eta_s = kc + \ln \eta_o$$

Now $\log \eta_o$ is a constant, say ϕ , at the constant temperature and for the same particular solvent. Hence

$$\ln \eta_s = \theta c + \phi.$$

In this paper an attempt has been made to ascertain if the above equations of Taimini are also applicable to the concentrated and supersaturated solutions of non-electrolytes in non-aqueous solvents.

EXPERIMENTAL

The method employed was that of Chatterji and Ram Gopal (*J. Indian Chem. Soc.*, 1947, **24**, 279) which essentially was the modified form of Scarpa's method. The viscosity was determined at five different concentrations and at various temperatures. For brevity of space the observations at only two different temperatures, lowest and highest, are recorded below. The concentrations are given in grams of anhydrous solute in 100 grams of pure solvent.

TABLE I

Viscosity and concentration

Solvent	Solute.	Temp.	Viscosity at different concentrations				
			$c =$	15.66	20.00	25.50	32.00
Hexane	Naphthalene	30°	0.003636	0.003813	0.003926	0.004135	...
		45°	0.003166	0.003268	0.003406	0.003567	0.003785
		$c =$	7.20	9.83	12.50	33.33	86.85
„	Diphenyl-amine	30°	0.003520	0.003675	0.003824	0.005085	0.015300
		45°	0.003079	0.003164	0.003288	0.004182	0.007796
		$c =$	54.00	59.00	82.00	92.00	118.00
Benzene	Naphthalene	30°	0.008077	0.008211	0.008740	0.009452	...
		45°	0.006540	0.006660	0.007066	0.007546	0.008170
		$c =$	66.40	75.60	90.80	112.80	138.00
„	<i>p</i> -Dibromo-benzene	30°	0.007506	0.007715	0.008051	0.008631	...
		40°	0.006593	0.006739	0.007021	0.007521	0.008016
		$c =$	21.20	35.10	49.20	66.60	85.20
„	<i>m</i> -Dinitro-benzene	30°	0.006997	0.008048	0.009130	0.010540	...
		45°	0.005698	0.006477	0.007265	0.008286	0.009624
		$c =$	9.648	11.73	14.48	18.34	21.96
„	Benzoic acid	35°	0.005991	0.006160	0.006421	0.006626	...
		45°	0.005267	0.005401	0.005600	0.005832	0.006100
		$c =$	66.00	82.00	100.00	127.00	162.00
Toluene	Naphthalene	40°	0.007058	0.007571	0.007946
		50°	0.006270	0.006720	0.007058	0.007534	0.008217
		$c =$	24.50	28.00	33.50	40.00	47.00
„	Acenaph-thene	30°	0.006888	0.007125	0.007479	0.007940	...
		45°	0.005730	0.005931	0.006035	0.006516	0.006900
		$c =$	182.50	280.00	487.00	830.00	...
„	<i>o</i> -Nitro-phenol	40°	0.018800	0.013430	0.016720	0.020160	...
		50°	0.009420	0.011360	0.014110	0.016740	...
		$c =$	28.00	45.97	56.45	75.00	...
CCl ₄	Naphthalene	40°	0.009335	0.010450	0.011090
		50°	0.008138	0.009072	0.009672	0.009974	...
		$c =$	24.20	27.00	36.50	34.00	39.00
CHCl ₃	Acenaph-thene	25°	0.008920	0.009020	0.009340	0.009695	...
		40°	0.007199	0.007426	0.007610	0.007968	0.008631
		$c =$	28.52	33.32	40.80	49.26	56.60
„	<i>m</i> -Dinitro-benzene	25°	0.010280	0.011080	0.012230
		40°	0.008356	0.008885	0.009900	0.011320	0.012130
		$c =$	62.00	76.00	90.00	112.00	136.00
Chloro-benzene	Naphthalene	45°	0.008436	0.008870	0.009220	0.009695	0.010190
		55°	0.007505	0.007816	0.008141	0.008553	0.008936

TABLE I (contd.)

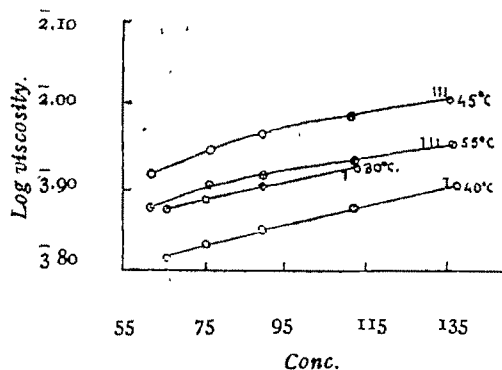
Solvent.	Solute.	Temp.	Viscosity at different concentrations				
Bromo-benzene	<i>m</i> -Dinitro-benzene	35°	<i>c</i> = 19.40	32.60	39.40	49.30	54.40
		45°	0.012210	0.013910	0.015610	0.017220	...
			0.010740	0.012130	0.013430	0.014720	0.015760
,,	<i>o</i> -Nitro-phenol	30°	<i>c</i> = 134.00	187.00	332.00	535.00	...
		50°	0.018840	0.021340	0.026400
			0.013500	0.014770	0.017730	0.019340	.
Aniline	Naphthalene	35°	<i>c</i> = 36.40	45.80	60.00	84.00	108.00
		55°	0.023650	0.022910	0.022240
			0.015300	0.015000	0.014750	0.014330	0.014170
Acetone	Naphthalene	30°	<i>c</i> = 44.83	56.00	68.00	84.00	100.00
		40°	0.004640	0.004914	0.005296	0.005790	0.006285
			0.004207	0.004423	0.004781	0.005170	0.005571
Acetone	<i>o</i> -Nitro-aniline	25°	<i>c</i> = 117.00	159.00	174.00	230.00	280.00
		40°	0.012290	0.015150	0.017420	0.022570	0.023660
			0.009826	0.012020	0.013520	0.017210	0.018170
Methyl alcohol	Acet-anilide	30°	<i>c</i> = 41.05	47.04	53.84	64.00	75.60
		40°	0.009180	0.009842	0.010570	0.011590	...
			0.007805	0.008320	0.008860	0.009662	0.011660
,,	Benzoic acid	30°	<i>c</i> = 68.00	74.00	83.00	93.00	...
		45°	0.011960	0.012900	0.013600
			0.009466	0.010020	0.010530	0.011330	...
,,	Urea	30°	<i>c</i> = 20.00	22.00	24.00	27.00	30.00
		45°	0.008914	0.009540	0.009945	0.010440	0.011110
			0.006933	0.007466	0.007656	0.008155	0.008588
Propyl alcohol	Benzoic acid	30°	<i>c</i> = 40.00	44.00	50.00	56.00	...
		45°	0.025310	0.026030	0.027340	0.028440	...
			0.017700	0.018160	0.018810	0.019650	...
<i>iso</i> Propyl alcohol	<i>p</i> -Dibromo-benzene	30°	<i>c</i> = 8.00	11.52	14.96	18.00	...
		45°	0.017130	0.016630	0.016770	0.016820	...
			0.011610	0.011420	0.011500	0.011600	...
<i>n</i> -Butyl alcohol	Naphthalene	40°	<i>c</i> = 12.00	14.95	18.23	23.00	29.00
		50°	0.016700	0.016330	0.016240	0.016010	0.015670
			0.013300	0.013120	0.013000	0.012800	0.012600
Acetic acid	Naphthalene	40°	<i>c</i> = 15.51	20.91	28.00	36.00	48.00
		55°	0.010100	0.010230	0.010240	0.010490	...
			0.008163	0.008190	0.008243	0.008373	0.008481

DISCUSSION

From the results given above the following types of curves have been plotted :
 (a) viscosity against concentration, (b) log viscosity against concentration. Of these two types of curves, log viscosity against concentration gives a more general and

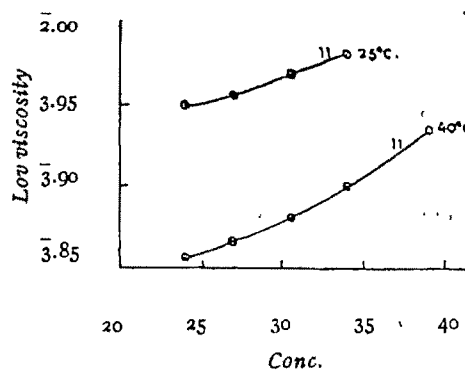
clearer approach to linearity, hence only a few of these curves are given as typical examples. The plotted curves can be divided into three categories viz., (i) those which

FIG. 1



I. Benzene-*p*-dibromobenzene.
III. Chlorobenzene-naphthalene.

FIG. 2

II. CHCl_3 -acenaphthene.

give a straight line, (ii) those giving a curve with positive curvature, and (iii) those giving a negative curvature. Results are given in Table II.

TABLE II

Results of plot of log viscosity against concentration

Straight line.		Curve with a positive curvature.		Curve with a negative curvature.	
Solvent.	Solute.	Solvent.	Solute.	Solvent.	Solute.
1. Hexane	Naphthalene	Acetic acid	Naphthalene	Chlorobenzene	Naphthalene
2. „	Diphenylamine	Chloroform	Acenaphthene	Toluene	<i>o</i> -Nitrophenol
3. Benzene	Naphthalene	„	<i>m</i> -Dinitrobenzene	Bromobenzene	<i>o</i> -Nitrophenol
4. „	<i>p</i> -Dibromobenzene	Aniline	Naphthalene	Acetone	<i>o</i> -Nitroaniline
5. „	<i>m</i> -Dinitrobenzene				
6. „	Benzoic acid				
7. Toluene	Naphthalene				
8. „	Acenaphthene				
9. CCl_4	Naphthalene				
10. Bromobenzene	<i>m</i> -Dinitrobenzene				
11. Acetone	Naphthalene				
12. MeOH	Acetanilide				
13. „	Benzoic acid				
14. „	Urea				
15. Propyl alcohol	Benzoic acid				

From the results recorded above it is found that the second equation of Taimini is generally obeyed by most of these solutions. At low temperatures there is a little curvature in some cases but at high temperature the curvature almost disappears and the curve merges into a straight line. If we consider two concentrations c_1 and c_2 , then the above equation becomes

$$\begin{aligned} \ln \eta_1 &= \theta c_1 + \phi \\ \text{and } \ln \eta_2 &= \theta c_2 + \phi \\ \text{or } \theta &= \frac{\ln \eta_2 - \ln \eta_1}{c_2 - c_1} \end{aligned}$$

i.e. ' θ ' denotes the change in viscosity per gram of solute. From the value of θ , which depends on the degree of solvation, a rough idea of relative solvation of different substances can be obtained. The greater the value of θ , higher is the solvation. Now, if in the above equation of Taimini, the concentration of the solute is taken to be zero, then we get

$$\ln \eta = \phi$$

i.e. ' η ' of pure solvent can be obtained.

The values of θ and ϕ have been calculated for the solutions which give a straight line plot for $\ln \eta = \theta c + \phi$. The results for θ and ϕ are given in Table III.

TABLE III

Solvent	Solute	Temp.	θ	ϕ	η (calc.)
1. Hexane	Naphthalene	45°	3.09×10^{-3}	3.4524	0.002834
2. „	Diphenylamine	45°	6.18	3.4379	0.002759
5. Benzene	Naphthalene	45°	1.58	3.7303	0.005374
4. „	<i>p</i> -Dibromobenzene	40°	1.17	3.7400	0.005495
5. „	<i>m</i> -Dinitrobenzene	45°	3.56	3.6868	0.004862
6. „	Benzoic acid	45°	5.19	3.6718	0.004696
7. Toluene	Naphthalene	45°	1.96	3.6923	0.004910
8. „	Acenaphthene	45°	4.31	3.6523	0.004490
9. CCl ₄	Naphthalene	50°	2.62	3.8181	0.006580
10. Bromobenzene	<i>m</i> -Dinitrobenzene	45°	4.84	3.9362	0.008650
11. Aniline	Naphthalene	55°	9.04×10^{-4}	2.1878	0.015410
12. Acetone	Naphthalene	40°	1.94×10^{-3}	3.5366	0.003440
13. MeOH	Acetanilide	40°	4.62 „	3.7032	0.005050
14. „	Benzoic acid	45°	4.10 „	3.6974	0.004982
15. „	Urea	45°	1.60×10^{-3}	3.5189	0.003303
16. Propyl alcohol	Benzoic acid	45°	2.77×10^{-3}	2.1371	0.013710
17. <i>iso</i> Propyl alcohol	<i>p</i> -Dibromobenzene	45°	1.13 „	2.0775	0.011960
18. <i>n</i> -Butyl alcohol	Naphthalene	50°	1.30 „	2.1374	0.013720

C O N C L U S I O N

From the results given above it is found that

1. For the solutions of toluene-naphthalene, carbon tetrachloride-naphthalene, benzene-benzoic acid and aniline-naphthalene the experimental and the calculated values of viscosity differ within 1%.

2. For the solutions of benzene-*m*-dinitrobenzene, *isopropyl* alcohol-*p*-dibromobenzene and butyl alcohol-naphthalene the difference between the calculated and the experimental value of viscosity is between 2% and 3%.

3. For the solutions of hexane-naphthalene, hexane-diphenylamine, benzene-naphthalene, toluene-naphthalene, methyl alcohol-acetanilide, and acetic acid-naphthalene the difference between the calculated and the experimental value of viscosity is between 5% and 10%.

4. For the solutions of acetone-naphthalene, methyl alcohol-urea, and methyl alcohol-benzoic acid the difference between the calculated and the experimental value of viscosity is above 10%.

In cases (1) and (2) the difference between the calculated and the experimental value of viscosity is much less than that in cases (3) and (4). It is probably due to the solvation being more marked in cases (3) and (4) than in cases (1) and (2).

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VARIATION OF ABSOLUTE VISCOSITY WITH TEMPERATURE. ORGANIC SOLUTES IN NON-AQUEOUS SOLVENTS

BY A. C. CHATTERJI AND A. N. BOSE

The viscosity of a fairly large number of systems of non-electrolytes in non-aqueous solvents has been studied at various temperatures. It has been shown that the simple Andrade's equation is applicable to most of the systems. The deviations can be explained by Rabinovich's solvate hypothesis and the depolymerisation hypothesis of Applebey.

The viscosity of a large number of non-electrolytes in non-aqueous solvents has been determined with a view to finding out if Andrade's equation is applicable to these systems. Many workers have applied successfully Andrade's equation to pure liquids and liquid melts. Recently several workers (Berl, Umstätter and Karrer, *Z. physikal. Chem.*, 1931, **162**, 284 ; Joshi and Solanki, *J. Indian Chem. Soc.*, 1940 **17**, 630 ; Ram Gopal, Ph. D. thesis, 1946, Lucknow University) have extended this equation to aqueous systems.

It has been generally assumed that the failure of the Andrade's equation is due either to the existence of polymerised molecules in the solvents or solvate complexes in the solutions. Another object of this investigation is to find out whether any sudden change in viscosity occurs when the solution passes from the saturated to the supersaturated region.

E X P E R I M E N T A L

The method employed was that of Chatterji and Ram Gopal (*J. Indian Chem. Soc.*, 1947, **24**, 455) which essentially was a modified form of Scarpa's method.

The viscosity was determined with five different concentrations and at several temperatures. But on account of brevity of space, the observations at the highest and the lowest concentrations have only been recorded below. The concentrations are in grams of anhydrous solute in 100 grams of pure solvent.

TABLE I
Viscosity of solutions at different temperatures.

Solvent.	Solute.	Conc.	25°	30°	35°	40°	45°	50°
Hexane	Naphthalene	15.66	0.003806	0.003636	0.003455	0.003310	0.003166	—
		32.00	—	0.004135	0.003922	0.003737	0.003567	—
	Diphenyl-amine	9.83 33.32	0.003866 —	0.003675 0.005085	0.003515 0.004768	0.003325 0.004472	0.003164 0.004182	— —
Benzene	Naphthalene.	54.00	0.008712	0.008077	0.007485	0.006983	0.006540	—
		92.00	—	0.009452	0.008742	0.008115	0.007546	—
,,	<i>p</i> -Dibromobenzene	75.60	0.008249	0.007715	0.007190	0.006739	—	—
		90.80	0.008532	0.008051	0.007502	0.007021	—	—
,,	<i>m</i> -Dinitrobenzene	35.12	0.008660	0.008048	0.007465	0.006980	0.006477	—
		66.40	—	0.010540	0.009737	0.009022	0.008286	—
,,	Benzoic acid	5.64	—	0.006414	0.005991	0.005625	0.005267	—
		18.34	—	—	0.006626	0.006220	0.005832	—

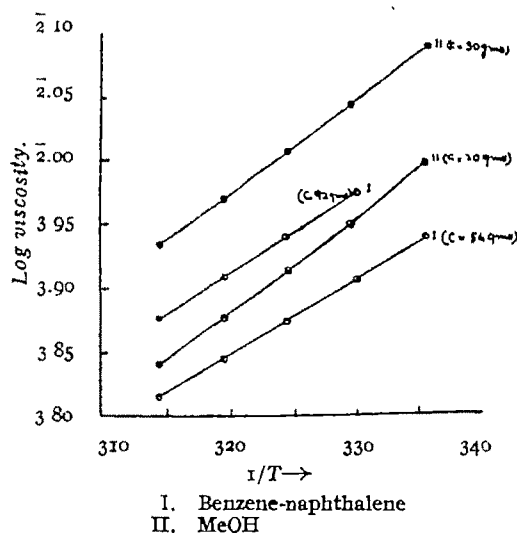
TABLE I (contd.).

Solvent.	Solute.	Conc.	25°	30°	35°	40°	45°	50°
Toluene	Naphthalene.	66.00	—	0.007855	0.007470	0.007058	0.006610	0.006270
		82.00	—	—	0.008101	0.007571	0.007105	0.006720
,,	Acenaphthene.	24.50	0.037330	0.006898	0.006467	0.006080	0.005730	—
		40.00	—	0.007940	0.007400	0.006961	0.006516	—
,,	o-Nitrophenol	182.50	—	0.012780	0.011820	0.010880	0.010110	0.009420
		487.00	—	—	0.018380	0.016720	0.015280	0.014110
CCl ₄	Naphthalene.	28.00	—	0.010850	0.010000	0.009335	0.008708	0.008138
		56.45	—	—	—	0.011090	0.010360	0.009672
,,	o-Nitroaniline	1.996	—	0.008952	0.008298	0.007841	0.007321	0.006886
		8.330	—	—	0.010000	0.009361	0.008740	0.008093
CHCl ₃	Acenaphthene	24.20	0.008920	0.008295	0.007764	0.007199	—	—
		34.00	0.009695	0.009070	0.008473	0.007968	—	—
,,	m-Dinitrobenzene	33.32	0.011080	0.010250	0.009550	0.008885	—	—
		40.80	0.012230	0.011370	0.010660	0.009900	—	—
Chlorobenzene	Naphthalene	62.00	—	—	0.009620	0.009041	0.008436	0.007981
		76.00	—	—	0.010110	0.009450	0.008870	0.008320
Bromobenzene	m-Dinitrobenzene	19.40	0.014160	0.013070	0.012210	0.011440	0.010740	—
		39.40	—	0.016750	0.015610	0.014400	0.013430	—
,,	o-Nitrophenol	134.00	—	0.018840	0.017190	0.015760	0.014600	0.013500
		535.00	—	—	0.026580	0.023660	0.021340	0.019340
Aniline	Naphthalene	36.40	—	—	0.023650	0.020920	0.018680	0.016870
		60.00	—	—	0.022240	0.019880	0.017830	0.016160
Nitrobenzene	,,	43.61	—	0.016460	0.015440	0.014400	0.013290	0.012310
		75.11	—	—	0.015780	0.014500	0.013460	0.012520
Acetone	,,	44.83	0.004870	0.004640	0.004428	0.004207	—	—
		68.00	0.005618	0.005296	0.005029	0.004781	—	—
,,	o-Nitroaniline	117.00	0.012290	0.011420	0.010590	0.009826	—	—
		280.00	0.023660	0.021750	0.019940	0.018170	—	—
MeOH	Acenaphthene.	2.25	0.005715	0.005301	0.004940	0.004598	0.004360	—
		3.50	—	0.005362	0.005036	0.004714	0.004405	—
,,	Acetanilide	41.05	0.009964	0.009180	0.008461	0.007805	—	—
		53.84	0.011580	0.010570	0.009716	0.008860	—	—
,,	Benzoic acid	68.00	0.013110	0.011960	0.010980	0.010140	0.009466	—
		83.00	—	0.013600	0.012500	0.011470	0.010530	—
,,	Diphenylamine	20.00	0.008140	0.007390	0.006818	0.006313	0.005840	—
		39.40	0.010120	0.009262	0.008495	0.007809	0.007151	—
,,	Urea	20.00	0.009735	0.008914	0.008215	0.007546	0.006923	—
		30.00	0.012220	0.011110	0.010190	0.009311	0.008588	—
Propyl alcohol	Benzoic acid.	40.00	0.028920	0.025310	0.022430	0.019880	0.017700	—
		56.00	—	0.028440	0.024980	0.022060	0.019650	—
,,	Urea	2.56	0.021600	0.018960	0.016910	0.015020	0.013390	—
		4.00	0.022400	0.020030	0.017680	0.015680	0.014010	—
isoPropyl alcohol	p-Dibromobenzene	11.52	0.019450	0.016820	0.014760	0.013070	0.011600	—
		18.00	—	0.016630	0.014700	0.012910	0.011420	—
n-Butyl alcohol	Naphthalene	14.95	—	0.020760	0.018480	0.016330	0.014610	0.013120
		23.00	—	—	0.017960	0.016010	0.014270	0.012800
Acetic acid	,,	15.51	—	0.011870	0.010930	0.010100	0.009386	0.008751
		28.00	—	—	0.011080	0.010240	0.009510	0.008838

DISCUSSION

From the results given above the following types of curves have been plotted: (a)

FIG. 1



viscosity—temperature, (b) log viscosity—temperature, (c) log viscosity— $1/T$. Of these types of curves, log viscosity against $1/T$ gives a more general and clearer approach to linearity, hence only a few of these curves are given as typical examples. The plotted curves can be divided into two categories: (i) those that give straight lines, (ii) those that do not give straight lines. The results are given below.

TABLE II

Results obtained by plotting log viscosity against $1/T$.

Straight line		Not straight line.	
Solvent.	Solute.	Solvent.	Solute.
1. Toluene	Naphthalene	1. Methyl alcohol	Acenaphthene
2. "	Acenaphthene	2. " "	Acetanilide
3. "	<i>o</i> -Nitrophenol	3. " "	Urea
4. Hexane	Naphthalene	4. " "	Diphenylamine
5. "	Diphenylamine	5. " "	Benzoic acid
6. Benzene	Naphthalene	6. Propyl alcohol	Urea
7. "	<i>p</i> -Dibromobenzene	7. <i>iso</i> Propyl alcohol	<i>p</i> -Dibromobenzene
8. "	<i>m</i> -Dinitrobenzene		
9. "	Benzoic acid		
10. CCl_4	Naphthalene		
11. "	<i>o</i> -Nitroaniline		
12. $CHCl_3$	Acenaphthene		
13. "	<i>m</i> -Dinitrobenzene		
14. Chlorobenzene	Naphthalene		
15. Bromo- "	<i>m</i> -Dinitrobenzene		
16. " "	<i>o</i> -Nitrophenol		
17. Aniline	Naphthalene		
18. Nitrobenzene	"		
19. Acetone	"		
20. Acetic acid	"		
21. Propyl alcohol	Benzoic acid		
22. <i>n</i> -Butyl alcohol	Naphthalene		

From the results it is clear that the substances which dissolve to produce highly viscous solutions show a deviation from the linearity and also the solutions of associated solvents generally do not give a straight line plot except the systems propyl alcohol-benzoic acid, *n*-butyl alcohol-naphthalene.

The simple Andrade's equation $\ln \eta = A + B/T$ meant for non-associated pure liquids is applicable to most of the non-electrolytes in non-associated solvents examined here, which means that the solutions behave almost as non-associated liquids in this respect.

Moreover, when the constants A and B are calculated, the results obtained are almost the same as in aqueous solutions. The value of A is nearly constant and has the same numerical values as those for aqueous solutions, which means that at very high temperatures all solutions, whether aqueous or non-aqueous, approach a constant value for viscosity. Only in those cases, where the solvent has a chance of being associated, such as alcohols, the value of A is slightly higher than the rest. As regards B in non-aqueous solutions, also we find that its value can be put into three categories. The value of B is between (i) 900 and 1500, (ii) 1500 and 2000, (iii) above 2000, as in the case of aqueous solutions of electrolytes. The results of A and B are given in Table III.

TABLE III

Solvent	Solute.	A .	B (Q/R)	Solvent	Solute.	A .	B (Q/R)
1. Hexane	Naphthalene	-5.4400	932.3	16. CCl ₄	<i>o</i> -Nitro-aniline	-6.6784	1438.0
2. Acetone	"	-5.5391	990.2	17. Acetone	"	-6.6784	1438.0
3. Hexane	Diphenyl-amine	-5.9833	1065.0	18. Methyl-alcohol	Diphenyl-amine	-7.0064	1513.0
4. Toluene	Naphthalene	-5.6413	1092.0	19. "	Benzoic acid	-6.8969	1540.0
5. Chloro-benzene	"	-5.8607	1195.0	20. Acetic acid	Naphthalene	-6.8984	1540.0
6. Toluene	Acenaphthene	-6.0181	1192.0	21. Methyl alcohol	Acetanilide	-7.0876	1557.0
7. Benzene	Benzoic acid	-6.1510	1221.0	22. Toluene	<i>o</i> -Nitrophenol	-7.1260	1642.0
8. "	<i>p</i> -Dibromobenzene	-6.1574	1248.0	23. Bromobenzene	"	-7.1347	1670.0
9. Bromobenzene	<i>m</i> -Dinitrobenzene	-6.2957	1251.0	24. Methyl alcohol	Urea	-7.3713	1642.0
10. Benzene	Naphthalene	-6.4252	1336.0	25. Chloroform	Acenaphthene	-7.6628	1727.0
11. "	<i>m</i> -Dinitrobenzene	-6.4261	1336.0	26. Aniline	Naphthalene	-8.6345	2176.0
12. CCl ₄	Naphthalene	-6.3009	1337.0	27. Propyl alcohol	Urea	-9.1434	2291.0
13. Nitrobenzene	"	-6.1363	1354.0	28. "	Benzoic acid	-9.2216	2353.0
14. Methyl alcohol	Acenaphthene	-6.7354	1377.0	29. <i>iso</i> -"	<i>p</i> -Dibromobenzene	-9.4040	2353.0
15. Chloroform	<i>m</i> -Dinitrobenzene	-6.5054	1394.0	30. <i>n</i> -Butyl alcohol	Naphthalene	-9.4060	2385.0

To the first two categories the Andrade's equation is applicable, except for a few alcoholic solutions, as they give a straight line plot for log viscosity against $1/T$. The substances of the second category having the value of B between 1500 and 2000 show a tendency of forming solvates. Greater solvation will require greater shearing stress and therefore the value of B is large in the second category than in the first where the viscosity is low. In category three, the viscosity is considerably high and therefore the value of B is correspondingly high.

The system benzoic acid-propyl alcohol gives a comparatively high linear relation than benzoic acid in methyl alcohol. This may be due to two reasons, firstly the association in propyl alcohol is less than in methyl alcohol, secondly benzoic acid may be able to depolymerise the slightly associated propyl alcohol, but not methyl alcohol, which is more associated.

STUDIES IN SOME AROMATIC SULPHIDES AND THEIR DERIVATIVES

By A. V. REGE, J. W. AIRAN AND S. V. SHAH

Several aromatic sulphides have been treated with various reagents to determine the strength of the sulphur linkage in aromatic sulphides.

The reactions between benzene and naphthalene derivatives and chlorides of sulphur viz., sulphur mono- and dichloride and thionyl chloride have been studied by various workers and in most cases aromatic sulphides have been obtained (Onufrowicz, *Ber.*, 1890, **23**, 3355; Hirve *et al.*, *J. Univ. Bom.*, 1933, **2**, 128; 1934, **3**, 551; *J. Amer. Chem. Soc.*, 1935, **57**, 101; Airan and Shah, *J. Univ. Bom.*, 1940, **9**, 115). In order to determine the strength of the sulphur linkage on the one hand, and to ascertain the position of the same on the other, these sulphides have been treated with different reagents such as concentrated ammonia, cuprous chloride, silver nitrate, potassium dichromate and sulphuric acid, nitric acid (either dilute or concentrated or fuming) and bromine (the same references as above).

However, no particular author has made any attempt to study the strength of the sulphur linkage in the aromatic sulphides in a systematic manner. In this paper an attempt in such a direction has been made. Nitric acid (dilute and concentrated), bromine (in calculated quantities and in excess), chlorine, sulphuryl chloride and diazobenzene chloride have been allowed to react with the following aromatic sulphides and their acetyl derivatives. In those cases where the action of the above reagents on the following compounds has already been studied previously, it has not been repeated here.

- (1) 3:3'-Dicarboxy-4:4'-dihydroxydiphenyl sulphide (Hirve *et al.*, *J. Amer. Chem. Soc.*, 1935, **57**, 101).
- (2) 4:4'-Dihydroxydinaphthyl trisulphide (Onufrowicz, *loc. cit.*).
- (3) 3:3'-Diacyl-4:4'-dihydroxydinaphthyl sulphide (Airan and Shah, *loc. cit.*).
- (4) 3:3'-Dicarboxy-4:4'-dihydroxydinaphthyl sulphide (Airan and Shah, *loc. cit.*).
- (5) 2:2'-Dihydroxydinaphthyl sulphide (Onufrowicz, *loc. cit.*).
- (6) 2:2'-Dihydroxy-3:3'-dicarboxydinaphthyl sulphide (Airan and Shah, *loc. cit.*).
- (7-12) Acetyl derivatives of the above.

EXPERIMENTAL

(A.V. Rege carried out the experimental part of this work.)

The reaction between sulphuryl chloride and the sulphide was carried out in dry benzene by refluxing the mixture for about 1 hour at 50°-60°.

Chlorination, bromination and nitration (dilute nitric acid) were carried out in acetic acid solution of the sulphides and their acetyl derivatives.

Diazobenzene chloride was prepared according to the method described by Shah and co-workers (*J. Univ. Bom.*, 1943, **11**, 85). The reactions were carried out in sodium hydroxide solutions of the sulphides and sodium bicarbonate solutions of their acetyl derivatives.

The results are shown in the following table.

TABLE I

The sulphide.	Reagent.	Product.	M. p	Remarks.
(1) 3:3'-Dicarboxy-4:4'-dihydroxydiphenyl sulphide (2g.)	Sulphuryl chloride (5 c.c.)	5-Chlorosalicylic acid	167°	Known (Smith, <i>Ber.</i> 1878 11, 1225)
Do	Cl ₂	3:5-Dichlorosalicylic acid	214°	Known (Smith <i>loc.cit.</i>)
Do	Diazobenzene chloride	5-Benzeneazo-salicylic acid	214°	Known (Zibell, <i>Ber.</i> , 1891, 25, 1696)
(2) 4:4'-Dihydroxy-dinaphthyl trisulphide (2g.)	Sulphuryl chloride (5 c.c.)	4-Chloronaphthol	116°	Known (Shah, <i>J. Univ. Bom.</i> , 1942, 10, 134)
Do	Cl ₂	2:4-Dichloro- α -naphthol	101°	Known (Cleve, <i>Ber.</i> , 1888, 21, 891)
Do	Br ₂ (2 c.c.)	2:4-Dibromo- α -naphthol	108°	Known (Biedermann, <i>Ber.</i> , 1873, 6, 1119)
Do	HNO ₃ (dil. & conc.)	A plastic mass	—	—
Do	Diazobenzene chloride	4-Benzeneazo- α -naphthol	205°	Known (Typke, <i>Ber.</i> , 1877, 10, 1580)
(3) 3:3'-Diacyl-4:4'-dihydroxydinaphthyl sulphide	Cl ₂	4-Chloro-2-acetyl- α -naphthol	117°	Known (Shah, <i>J. Univ. Bom.</i> , 1942, 10, 132)
Do	Cl ₂ (excess)	Trichloromethyl-(4-chloro-1-hydroxy)- β -naphthyl ketone	141°	New
Do	Br ₂ (1 c.c.)	4-Bromo-2-acetyl- α -naphthol	126°	Known (Hantzsch, <i>Ber.</i> , 1906, 39, 3097)
Do (2g.)	Br ₂ (4 c.c.)	Dibromomethyl (4-bromo-1-hydroxy)- β -naphthyl ketone.	201°	New
Do (2g.)	HNO ₃ (conc., 3 c.c.)	4-Nitro-2-acetyl- α -naphthol	154°	Known (Shah, <i>J. Univ. Bom.</i> , 1940, 9, 115)
(4) 3:3'-Dicarboxy-4:4'-dihydroxydinaphthyl sulphide	Cl ₂	4-Chloro-1-oxy-2-naphthoic acid	229°	Known (Weil, <i>Ber.</i> , 1911, 44, 3061)
Do	Cl ₂ (excess)	2:2:3:4:4-Pentachloro-1-oxy-naphthalene tetrahydride	152°	Known (Zincke, <i>Ber.</i> , 1888, 21, 1044)
Do (2g.)	Br ₂ (5 c.c.)	4-Bromo-1-oxy-2-naphthoic acid	241°	Known (Weil, <i>Ber.</i> , 1911, 44, 2700)
Do (2g.)	HNO ₃ (conc., 4 c.c.)	2:4-Dinitro- α -naphthol	137°	Known (Shah, <i>J. Univ. Bom.</i> , 1940, 9, 115)
(5) 2:2'-Dihydroxy-dinaphthyl sulphide (2 g.)	Sulphuryl chloride (5 c.c.)	1-Chloro- β -naphthol	70°	Known (Armstrong, <i>Chem. News</i> , 1889, 59, 225)
Do	Cl ₂	Do	70°	Do
(6) 2:2'-Dihydroxy-3:3'-dicarboxydinaphthyl sulphide	Cl ₂	1-Chloro-2-oxy-3-naphthoic acid	230°	Known (Gradenwitz, <i>Ber.</i> , 1894, 27, 2622)
Do	Cl ₂ (excess)	1:1:3:3:4-Pentachloro-2-oxynaphthalene tetrahydride	114°	Known (Zincke, <i>Ber.</i> , 1888, 21, 3379)
Do (5 g.)	Br ₂ (excess, 12c.c.)	1:6-Dibromo-2-oxy-3-naphthoic acid	251°	New
Do (2 g.)	HNO ₃ (conc., 5 c.c.)	1-Nitro-2-hydroxy 3-naphthoic acid	230°	Known (Shah, <i>J. Univ. Bom.</i> , 1940, 9, 115)

TABLE I (contd.)

The sulphide.	Reagent.	Product.	M. p.	Remarks.
(7) 3:3'-Dicarboxy-4:4'-diacetoxydiphenyl sulphide (2 g.)	Sulphuryl chloride (5 c.c.)	Original compound	—	No reaction.
Do	Cl ₂	Do		Do
Do (5 g.)	Br ₂ (6 c.c.)	3:3'-Dibromo-4:4'-diacetoxy-5:5'-dicarboxy-diphenyl sulphide	276°	Known (Hirve, <i>J. Amer. Chem. Soc.</i> , 1935, 57, 101)
Do (2 g.)	HNO ₃ (dil., 4 c.c.)	5-Nitrosalicylic acid	221°	Known, Do
Do (5 g.)	HNO ₃ (conc., 10 c.c.)	2:4:6-Trinitrophenol	120°	Known, Do
Do	Diazobenzene chloride	2:4:6-Tribenzeneazo phenol	215°	Known (Grandmougin, <i>Ber.</i> , 1907, 40, 3450)
(8) 4:4'-Diacetoxydinaphthyl sulphide (2 g.)	Sulphuryl chloride (5 c.c.)	Original compound		No reaction
Do	Cl ₂	Do		Do
Do (2 g.)	Br ₂ (8 c.c.)	A plastic mass		
Do (5 g.)	HNO ₃ (10 c.c.)	Do		
(9) 3:3'-Diacetyl-4:4'-diacetoxydinaphthyl sulphide (2 g.)	Sulphuryl chloride (5 c.c.)	Original compound		Do
Do	Cl ₂	Do		Do
Do (2 g.)	Br ₂ (5 c.c.)	Dibromomethyl-(4-bromo-1-hydroxy-) β -naphthyl ketone	201°	New
Do (2 g.)	HNO ₃ (dil. 5 c.c.)	4-Nitro-2-acetyl- α -naphthol	154°	Known (Shah, <i>J. Univ. Bom.</i> , 1940, 9, 115)
(9) 3:3'-Diacetyl-4:4'-diacetoxydinaphthyl sulphide	HNO ₃ (conc., 4 c.c.)	4-Nitro-2-acetyl- α -naphthol	154°	Known (Shah, <i>J. Univ. Bom.</i> , 1940, 9, 115)
(10) 3:3'-Dicarboxy-4:4'-diacetoxydinaphthyl sulphide (2 g.)	Sulphuryl chloride (3 c.c.)	Original compound		No action
Do	Cl ₂	Do		Do
Do (2 g.)	Br ₂ (5 c.c.)	4-Bromo-1-oxy-2-naphthoic acid	241°	Known (Weil, <i>Ber.</i> , 1911, 44, 2700)
Do (2 g.)	HNO ₃ (dil., 6 c.c.)	2:4-Dinitro- α -naphthol	136°	Known (Shah, <i>J. Univ. Bom.</i> , 1940, 9, 115)
Do (2 g.)	HNO ₃ (conc., 5 c.c.)	Do	Do	Do
Do	Diazobenzene chloride	4-Benzeneazo-1-oxy-2-naphthoic acid	192°	Known (Neitzki, <i>Ber.</i> 1887, 20, 1275)
(11) 2:2'-Diacetoxydinaphthyl sulphide (2 g.)	Sulphuryl chloride (5 c.c.)	Original compound		No reaction.
Do	Cl ₂	2:2'-Diacetoxy-6:6'-dichlorodinaphthyl sulphide	198°	New
		2:2'-Dihydroxy-6:6'-dichlorodinaphthyl sulphide (after hydrolysis of the above compound)	224°	New
Do (5 g.)	Br ₂ (10 c.c.)	2:2'-Dihydroxy-6:6'-dibromodinaphthyl sulphide	201°	New
		2:2'-Dihydroxy-6:6'-dibromodinaphthyl sulphide (after hydrolysis of the above compound)	224°	New

TABLE I (contd.)

The sulphide.	Reagent.	Product.	M.p.	Remarks.
2:2'-Dihydroxy-6:6'-dibromodinaphthyl sulphide (2 g.)	Br ₂ (0.8 c.c.)	1:6-Dibromo- β -naphthol	124°	Known
Do (2 g.)	HNO ₃ (dil., 7 c.c.)	2:2'-Diacetoxy-6:6'-dinitrodinaphthyl sulphide	210°	New
Do (4 g.)	HNO ₃ (conc., 10 c.c.)	Do	Do	Do
(12) 2:2'-Diacetoxy-3:3'-dicarboxydinaphthyl sulphide (2 g.)	Sulphuryl chloride (5 c.c.)	Original compound		No reaction
Do	Cl ₂	Do		Do
Do (5 g.)	Br ₂ (12 c.c.)	1:6-Dibromo-2-oxy-3-naphthoic acid	251°	New
Do (2 g.)	HNO ₃ (dil., 5 c.c.)	2:2'-Diacetoxy-3:3'-dicarboxy-6:6'-dinitrodinaphthyl sulphide	Did not melt up to 300°	New
2:2'-Diacetoxy-3:3'-dicarboxydinaphthyl sulphide (2 g.)	HNO ₃ (conc., 5 c.c.)	2:2'-Diacetoxy-3:3'-dicarboxy-6:6'-dinitrodinaphthyl sulphide	Did not melt up to 330°	New
Do	Diazobenzene chloride	2:2'-Dihydroxy-3:3'-dicarboxy-6:6'-dibenz-neazo-dinaphthyl sulphide	300°	New

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RAJARAM COLLEGE, KOLHAPUR.

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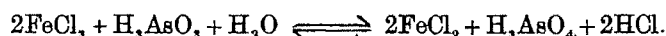
STUDIES IN THE COMPOSITION OF FERRIC ARSENITE AND FERROUS ARSENATE: PART I. QUALITATIVE STUDY OF THE REACTION BETWEEN FERRIC CHLORIDE AND SODIUM ARSENITE

BY ABANI K. BHATTACHARYA

By reacting ferric chloride with sodium arsenite in aqueous and neutralised and acidified solutions interesting evidences have been obtained of intermediate reactions between the reactants. The most important factors which govern the composition of ferric arsenite are : (i) the oxidation-reduction phenomenon between the reactants, (ii) H⁺-ion concentration of the system, (iii) hydrolytic character of the compound, and (iv) the phenomenon of adsorption.

The composition of ferric arsenite according to the chemical equation should correspond to the formula Fe(AsO₂)₃ when FeCl₃ is added to NaAsO₂. But in the literature more complex and variable formulae have been given e.g. 6K₂O, 5Fe₂O₃, 9As₂O₃, 24H₂O (Dobbin, *Pharm. J.*, 1904, *iv*, 81, 588), XFe(OH)₃, YAs₂O₃ (Oryng, *Kolloid Z.*, 1918, 22, 149) and Fe₄As₂O₁₅, 5H₂O or 3Fe₂O₃, Fe₂(AsO₃)₂, 5H₂O (Bunsen and Berthold : Mellor, "Treatise on Inorganic Chemistry", 1929, Vol. IX, p. 133).

The possibility of mutual oxidation and reduction was, however, suggested by Jellinek and Winogradoff (*Z. Electrochem.*, 1924, 30, 477) according to the following equation,



The above possibility of mutual oxidation and reduction suggests that the composition of ferric arsenite will be more or less a mixed compound. The secondary reactions which may follow may be indicated at a first glance as given below :

- (i) $2\text{FeCl}_3 + \text{NaAsO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{FeCl}_2 + \text{NaCl} + \text{HCl} + \text{H}_3\text{AsO}_4$
- (ii) $3\text{FeCl}_2 + 2\text{H}_3\text{AsO}_4 \rightarrow \text{Fe}_3(\text{AsO}_4)_2 + 6\text{HCl}$
- (iii) $\text{FeCl}_3 + \text{H}_3\text{AsO}_4 \rightarrow \text{FeAsO}_4 + 3\text{HCl}$
- and (iv) $\text{FeCl}_2 + 2\text{NaAsO}_2 \rightarrow \text{Fe}(\text{AsO}_2)_2 + 2\text{NaCl}.$

The ionic equation showing the oxidation-reduction products may be represented thus :



In order to study the above possibilities a number of samples of ferric arsenite was prepared by mixing the aqueous neutralised and slightly acidified solutions of the reactants and the filtrate was thoroughly subjected to qualitative analysis in each case.

E X P E R I M E N T A L

1. Aqueous solutions of ferric chloride and sodium arsenite ($M/5$, $M/10$, $M/25$ and $M/50$) were prepared and mixed together in equivalent proportion. The filtrates were collected and tested. It was observed that the filtrates were neutral: ferrous and ferric, nil, and arsenite was left over in excess, but no arsenate.

2. Aqueous solutions of ferric chloride and neutralised solutions of sodium arsenite, both at the above concentrations, were mixed in equivalent proportion (1 mole of FeCl_3 to 3 moles of NaAsO_2). The filtrate was acidic, ferrous and ferric were both present, arsenite was in excess but arsenate was doubtful.

A few more interesting points regarding the precipitation of ferric arsenite were noted, according as the solutions were aqueous, neutralised sodium arsenite or acidic.

3. When aqueous solutions of FeCl_3 or NaAsO_2 were mixed together, sufficient Fe(OH)_3 was precipitated along with ferric arsenite, because of the free alkali in NaAsO_2 solution. The precipitation was immediate and deep brown in colour.

4. When aqueous solution of ferric chloride was mixed with neutralised solution of NaAsO_2 , a colloidal solution of ferric arsenite was first formed, which precipitated on keeping overnight. A brown supernatant layer of colloidal Fe(OH)_3 mixed with ferric arsenite was also observed.

5. When more than one equivalent of aqueous or acidified solution of ferric chloride was added to one equivalent of aqueous or neutralised solution of NaAsO_2 , a colloidal solution of ferric arsenite was first formed which precipitated gradually in a short time.

6. Several samples of ferric arsenite were prepared by mixing excess of acidified ferric chloride to neutralised NaAsO_2 . A colloidal solution was obtained. This was dialysed in a parchment paper bag and the dialysate was concentrated. The dialysate showed that both ferrous and arsenate ions were present.

After these preliminary qualitative tests quantitative estimations were made to find out whether the same amount of residual arsenite was left over, when the reactants were mixed in equivalent proportion, but at different dilutions. This would show the effect of hydrolysis on ferric arsenite.

TABLE I

Conc. of the reactants.		Initial amount. of AsO_2 .	Amount. of AsO_2 left over.	Amount. of AsO_2 used up by FeCl_3 .
1.	$M/1.3\text{-FeCl}_3 + M/1.3\text{-NaAsO}_2$	0.4253 g.	0.2341 g.	0.2012 g
2.	$M/5 + M/5$	0.4253	0.2352	0.190
3.	$M/10 + M/10$	0.4253	0.2402	0.1851
4.	$M/25 + M/25$	0.4253	0.2604	0.1649
5.	$M/50 + M/50$	0.4253	0.2882	0.1371

DISCUSSION

The qualitative results show that mutual oxidation and reduction of the reactants do take place when neutralised or acidified solutions are mixed together. Another interesting point to note is that the aqueous solutions of ferric chloride and sodium arsenite, on mixing, give a neutral filtrate, although taken separately, FeCl_3 is acidic and NaAsO_2 is strongly alkaline. The residual AsO_2 in the filtrate shows that the total quantity of ferric chloride is not utilised in forming ferric arsenite, probably due to (i) the formation of intermediate products by mutual oxidation and reduction of the reactants, and (ii) hydrolysis of ferric arsenite, an indication of which has been obtained quantitatively in the above table.

The mechanism of the reactions between the aqueous solutions of ferric chloride and sodium arsenite therefore does not seem to be only an one-stage process. It appears that there are several intermediate reactions which have been shown in the equations given below:

- (1) $\text{FeCl}_3 + 3\text{NaAsO}_2 = \text{Fe}(\text{AsO}_2)_3 + 3\text{NaCl}$
- (2) $\text{FeCl}_3 + 3\text{NaOH} = \text{Fe}(\text{OH})_3 + 3\text{NaCl}$
- (3) $4\text{FeCl}_3 + 2\text{NaAsO}_2 + 4\text{H}_2\text{O} = 4\text{FeCl}_2 + 2\text{NaCl} + 2\text{HCl} + 2\text{H}_3\text{AsO}_4$
- (4) $3\text{FeCl}_2 + 2\text{H}_3\text{AsO}_4 = \text{Fe}_3(\text{AsO}_4)_2 + 6\text{HCl}$
- (5) $13\text{NaAsO}_2 + 13\text{H}_2\text{O} = 13\text{NaOH} + 13\text{HAsO}_2$
- (6) $\text{FeCl}_2 + 2\text{NaOH} = \text{Fe}(\text{OH})_2 + 2\text{NaCl}$
- (7) $8\text{NaOH} + 8\text{HCl} = 8\text{NaCl} + 8\text{H}_2\text{O}$

Adding, $6\text{FeCl}_3 + 18\text{NaAsO}_2 + 9\text{H}_2\text{O} = \text{Fe}(\text{AsO}_2)_3 + \text{Fe}(\text{OH})_3 + \text{Fe}(\text{OH})_2 + \text{Fe}_3(\text{AsO}_4)_2 + 13\text{HAsO}_2 + 18\text{NaCl}$.

The foregoing scheme of chemical changes covers the range of observation made qualitatively in the case of aqueous solutions. The resultant equation shows that (a) there is no free acid or alkali, (b) there is enough of free HAsO_2 in the solution, and (c) ferric arsenite hydrolyses more in dilute solutions, with proportionate increase in free HAsO_2 as already observed.

But when neutralised NaAsO_2 is mixed with FeCl_3 , the chemical changes probably take place according to the following modifications:

- (1) $3\text{NaAsO}_2 + 3\text{H}_2\text{O} = 3\text{NaOH} + 3\text{HAsO}_2$ (hydrolysis)
- (2) $3\text{NaOH} + 3\text{HCl} = 3\text{NaCl} + 3\text{H}_2\text{O}$ (neutralised by adding HCl)
- (3) $\text{FeCl}_3 + 3\text{NaAsO}_2 = \text{Fe}(\text{AsO}_2)_3 + 3\text{NaCl}$ (unhydrolysed)
- (4) $6\text{FeCl}_3 + 3\text{HAsO}_2 + 6\text{H}_2\text{O} = 6\text{FeCl}_2 + 6\text{HCl} + 3\text{H}_3\text{AsO}_4$
- (5) $3\text{FeCl}_2 + 2\text{H}_3\text{AsO}_4 = \text{Fe}_3(\text{AsO}_4)_2 + 6\text{HCl}$

Adding, $7\text{FeCl}_3 + 6\text{NaAsO}_2 + 6\text{H}_2\text{O} = \text{Fe}(\text{AsO}_2)_3 + \text{Fe}_3(\text{AsO}_4)_2 + 6\text{NaCl} + 3\text{FeCl}_2 + 9\text{HCl} + \text{H}_3\text{AsO}_4$

The above scheme of reactions suggests that the required proportion of ferric chloride to sodium arsenite (neutralised) is 7:6. Hence, when FeCl_3 is added to NaAsO_2 in equivalent proportion i. e. in the ratio of 1:3, excess of ferric and ferrous ions will appear in the filtrate and this has actually been observed (*vide* experimental 2). Test for arsenate is readily obtained, but the formation of arsenate is favoured by adding an excess of acidified FeCl_3 (*vide* experimental 6).

In view of the observations made by qualitative analysis of the filtrates obtained by mixing ferric chloride and sodium arsenite under different conditions of H-ion concentration and dilution, it may be concluded that the mechanism of reaction is complicated by intermediate changes brought about by mutual oxidation and reduction, hydrolysis of the products formed and by adsorption. Quantitative analysis of the various samples of ferric arsenite prepared will be communicated in a future communication.

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CHEMICAL LABORATORIES,
AGRA COLLEGE, AGRA

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MAGNETO-CHEMICAL STUDIES IN VALENCY AND MOLECULAR CONSTITUTION. PART III. HETEROPOLY MOLYBDATES AND TUNGSTATES WITH POLYVALENT METAL ATOMS IN THE COMPLEX

BY PRIYADARANJAN RÂY, AJITSANKAR BHADURI AND BYOMKES SARMA

A number of compounds containing molybdic acid anhydride and various bi, ter, and quadrivalent metal oxides, besides alkali or alkaline earth metal oxides, described by earlier workers, were prepared and examined magneto-chemically with a view to determining their constitution and the valence state of the central metal atoms involved in their formation. A similar study of a complex sodium manganese paratungstate with quadrivalent manganese has also been made. The results have led to the conclusion that these compounds should be regarded as salts of 6-molybdenum heteropolyacid or its derivative, with the metal atoms forming the centre of octahedral co-ordination complexes either of the penetration or the associated type. Only in the case of the nickel compound which contains 9 MoO_3 for each nickel atom, a different formulation as a double salt of 6-molybdenum and 12-molybdenum heteropolyacids, or as a salt of a new 9-molybdenum heteropolyacid, has been necessary. Hence, all of these, with the exclusion of the above mentioned nickel compound, might be included in the class of silico-, phospho-, arseno-, iodo- or telluro-molybdates, as already suggested by Rosenheim. The tungsten compound also can be represented as a derivative of 6-tungsten heteropolyacid salt.

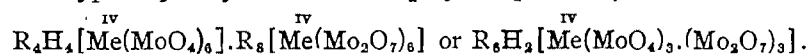
Heteropoly molybdates and tungstates with quadri- and quinquivalent metalloids like silicon, phosphorus and arsenic are quite well known. They are salts of the complex 12-molybdenum or 12-tungsten heteropolyacid of the general formula, $\text{H}_{12-n}[\text{Me}(\text{X}_2\text{O}_7)_6]_n\text{aq.}$, where $\text{X} = \text{Mo}$ or W . Iodine and tellurium also similarly form 6-molybdenum heteropolyacid complexes of the formula $\text{H}_6[\text{I}(\text{MoO}_4)_6]_n\text{aq.}$ and $\text{H}_6[\text{Te}(\text{MoO}_4)_6]_n\text{aq.}$, with septivalent iodine and sexivalent tellurium respectively. Besides, a large number of compounds containing molybdic acid anhydride and various tervalent metallic oxides, in addition to alkali metal and alkaline earth metal oxides, and in some cases even oxides of silver, mercury and lead, have been described by various workers (Struve, *J. prakt. Chem.*, 1854, i, 61 453; Friedheim and Keller, *Ber.*, 1906, 39, 4301; Markwald, Dissertation, Berlin, 1895; Hall, *J. Amer. Chem. Soc.*, 1907, 29, 692; Rosenheim and Schwer, *Z. anorg. Chem.*, 1914, 89, 224; Barbieri, *Atti. R. Accad. Lincei*, 1914, 23, 328; Kurnakow, *Chem. Ztg.*, 1899, 14, 113). They seem to form an isomorphous series of the general formula, $3\text{R}_2\text{O} \cdot \text{Me}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot x\text{H}_2\text{O}$. Compounds have also been described with oxides of metals in the quadrivalent state (Ni, Co and Mn) of the formula, $3\text{R}_2\text{O}(\text{RO}) \cdot \text{MeO}_2 \cdot 9\text{MoO}_3\text{aq.}$ (Hall, *loc. cit.*). Furthermore, compounds with oxides of metals in the bivalent state of the general formula, $3\text{R}_2\text{O} \cdot 2\text{MeO} \cdot 12\text{MoO}_3\text{aq.}$, ($\text{Me} = \text{Cu}, \text{Ni}, \text{Mn}, \text{Co}, \text{Mg}, \text{Ca}$), have also been prepared (Barbieri, *Atti. R. Accad. Lincei*, 1914, 23, II, 357; Marckwald, *loc. cit.* Rosenheim, *Z. anorg. Chem.*, 1916, 96, 147).

Some of the earlier workers (cf. Friedheim and Samelson, *Z. anorg. Chem.*, 1900, 24, 67) regarded these compounds as double molybdates, similar to double sulphates like alums. But the work of Hall (*loc. cit.*) and of Rosenheim (*loc. cit.*) have demonstrated that they should be represented as salts of complex inorganic acids composed of the oxide of the metal concerned and MoO_3 . They based their conclusion on the strong colour possessed by the compounds, the constant ratio of the oxide of the

heavy metal to MoO_3 in all their salts, the preparation of the free acid in some cases, and a study of the properties of the substances in aqueous solution. The complexes, composed of the oxides of the type, MeO and MeO_3 , were considered by Rosenheim as derivatives of paramolybdates, resembling the salts of 6-molybdenum heteropolyacids, like telluro- and iodomolybdic acids, in accordance with his view of the constitution of paramolybdates on the basis of Werner's theory. The constitution of these compounds were represented by him as follows :



Complexes with MeO_2 cannot, however, be represented either as salts of 6-molybdenum or 12-molybdenum heteropolyacid. They can, however, be regarded as double compounds of 6-molybdenum and 12-molybdenum heteropolyacid salts, or better as a new type of 9-molybdenum heteropoly complex salt, viz.



With a view to examining the nature of these complexes and the valency of their central metal atoms we have prepared a number of these complex metal molybdates, particularly those containing the metals of the first transitional series as the central atoms, and have measured their magnetic moments. Sodium, potassium and barium salts of a complex mangani-tungstic acid with quadrivalent manganese (Just, *Ber.*, 1903, **36**, 3619) have also been prepared and the magnetic susceptibility of the sodium salt determined. The results are described and discussed below.

EXPERIMENTAL

1. *Ammonium nickel^{IV} molybdate* was prepared according to the method described by Hall (*loc. cit.*) by oxidising a boiling solution of ammonium paramolybdate and nickel sulphate with ammonium persulphate. The substance was purified by recrystallising several times from hot water, containing a little ammonium persulphate. [Found: NH_3 , 6.30; Ni, 3.58; MoO_3 , 78.83; O(active), 0.975; H_2O (by diff.), 6.0. $3(\text{NH}_4)_2\text{O}.\text{NiO}_2.9\text{MoO}_3.5.5\text{H}_2\text{O}$ requires NH_3 , 6.21; Ni, 3.58; MoO_3 , 78.90; O(active), 0.974; H_2O , 6.03 per cent].

Magnetic susceptibility of the substance was measured by Gouy's method in a magnetic field of strength 10.16×10^3 gauss.

$$t = 24^\circ; \chi_g = -0.0571 \times 10^{-6}; \chi_M = -93.76 \times 10^{-6}.$$

After correction for diamagnetism, $\chi_A = 1.74 \times 10^{-6}$; $\mu_a = 0.065$.

The substance forms fine purple-black crystals.

The *barium salt* was prepared from a solution of the ammonium salt by precipitation with barium chloride. A brown crystalline precipitate was obtained. [Found. Ba, 20.14; Ni, 2.77; MoO_3 , 63.10; O(active), 0.769; H_2O (by difference from the loss by ignition and the amount of oxygen), 9.49. $3\text{BaO}.\text{NiO}_2.9\text{MoO}_3.11\text{H}_2\text{O}$ requires Ba, 20.14; Ni, 2.87; MoO_3 , 63.37; O(active), 0.782; H_2O , 9.68 per cent].

$$t = 30^\circ; \chi_g = -0.2001 \times 10^{-6}; \chi_M = -219.3 \times 10^{-6}; \chi_A = -41.5 \times 10^{-6}$$

2. *Potassium cobaltic^{III} molybdate* (6-MoO_3) was prepared by oxidising a boiling solution of a mixture of potassium paramolybdate and cobalt sulphate with potassium persulphate. The substance was purified by recrystallisation from hot water. [Found:

K, 9.16; Co, 4.47; MoO₃, 66.95; O(active), 0.57; H₂O (from total loss by ignition and that of oxygen), 15.70. 3K₂O, Co₂O₃, 12MoO₃, 22.5H₂O requires K, 9.08; Co, 4.58; MoO₃, 66.94; O(active), 0.62; H₂O, 15.67 per cent].

$t=30^{\circ}$; $\chi_g = -0.446 \times 10^{-6}$; $\chi_M = -115.1 \times 10^{-6}$; $\chi_A = 90.6 \times 10^{-6}$; $\mu_n = 0.58$.

The substance forms crystals of green colour. Hall (*loc. cit.*) obtained a different product by this method with quadrivalent cobalt of the composition, 3K₂O, CoO₂, 9MoO₃, 6.5H₂O.

3. *Potassium cobaltic^{III} molybdate* (5-MoO₃) was prepared from a boiling solution of cobalt acetate (3.5 g.), potassium paramolybdate (10 g.) and potassium persulphate (6 g.). The violet precipitate, formed at the beginning, dissolved on continuous heating. The green solution, so obtained, was freed from the suspended impurities by immediate filtration. The clear solution on cooling gave light green, sparingly soluble micro-crystals together with some white needles of potassium trimolybdate. The mixture was filtered and the white crystals of trimolybdate were removed by rubbing with the mother-liquor. The product was washed and dried as usual (cf. Friedheim and Keller, *loc. cit.*). [Found: K, 11.05; Co, 5.40; MoO₃, 67.48; O(active), 0.73; H₂O (from the loss of weight by ignition and that of oxygen), 11.60. 3K₂O, Co₂O₃, 10MoO₃, 13.5H₂O requires K, 11.0; Co, 5.46; MoO₃, 67.52; O(active), 0.74; H₂O, 11.54 per cent].

The substance was found to be diamagnetic. χ_g at $30^{\circ} = 0.0$; $\chi_A = +110 \times 10^{-6}$; $\mu_n = 0.52$.

The corresponding *ammonium salt* was prepared by treating a mixture of cobaltous acetate (1.55 g. in 40 c.c. water) and ammonium paramolybdate (7.5 g. in 30 c.c. water) with 10 c.c. of 18% hydrogen peroxide solution in the cold. The mixture was gently warmed when the solution became dark green at the end. On cooling, small quantities of 6-molybdenum compound were precipitated along with the dark green crystals. These latter were first separated by mechanical means and then by recrystallization from water at 70° . The crystals were washed and dried as usual (cf. Friedheim and Keller, *loc. cit.*). [Found: NH₃, 3.57; Co, 5.99; MoO₃, 73.84; O(active), 0.812; H₂O, (by diff.), 12.28. 2(NH₄)₂O, Co₂O₃, 10MoO₃, 12H₂O requires NH₃, 3.53; Co, 6.01; MoO₃, 74.78; O(active), 0.814; H₂O, 11.21 per cent].

$t=30^{\circ}$; $\chi_g = 0$; $\chi_A = +76 \times 10^{-6}$; $\mu_n = 0.43$.

4. *Ammonium chromic molybdate* was prepared by boiling a solution of ammonium chrome alum with ammonium paramolybdate. The rose-red crystalline product was recrystallized several times from hot water (cf. Hall, *loc. cit.*). [Found: NH₃, 4.61; Cr, 4.07; MoO₃, 67.81; H₂O (by diff.), 19.20. 3.5(NH₄)₂O, Cr₂O₃, 12MoO₃, 27H₂O requires NH₃, 4.67; Cr, 4.08; MoO₃, 67.77; H₂O, 19.07 per cent].

$t=31^{\circ}$; $\chi_g = 5.17 \times 10^{-6}$; $\chi_M = 12710 \times 10^{-6}$; $\chi_A = 6509 \times 10^{-6}$; $\mu_n = 4.0$.

5. *Ammonium ferric molybdate* was prepared from ammonium paramolybdate and ferric ammonium alum (cf. Hall, *loc. cit.*). The substance forms almost white crystals. [Found: NH₃, 4.32; Fe, 4.74; MoO₃, 72.80; H₂O (from total loss by ignition and the amount of ammonia), 13.96. 3(NH₄)₂O, Fe₂O₃, 12MoO₃, 11H₂O requires NH₃, 4.30; Fe, 4.73; MoO₃, 72.81; H₂O, 13.87 per cent].

$t=30^{\circ}$; $\chi_g = 11.73 \times 10^{-6}$; $\chi_M = 27790 \times 10^{-6}$; χ_A (corr.) = 14013.5×10^{-6} ; $\mu_n = 5.85$.

6. *Barium mangani^{IV}-molybdate* was prepared from a boiling solution of a mixture of potassium molybdate (4 g.), molybdic acid anhydride (6 g.), and hydrated manganese sulphate (1g.) by oxidation with bromine water. The excess of molybdic acid and other suspended impurities were removed by filtration. The clear solution, on cooling, deposited the crystals of potassium mangani-molybdate. A solution of this salt, on treatment with that of barium chloride, gave a light brown micro-crystalline precipitate of the barium salt. This was washed and dried as usual (cf. Hall, *loc. cit.*). [Found: Ba, 20.15; Mn, 2.60; MoO₃, 62.87; O(active), 0.753; H₂O (by diff.), 9.75. 3BaO, MnO₂, 9MoO₃, 12H₂O requires Ba, 20.13; Mn, 2.67; MoO₃, 62.98; O(active), 0.77; H₂O, 9.53 per cent].

$$t = 28^\circ; \chi_g = 2.93 \times 10^{-6}; \chi_u = 6036 \times 10^{-6}; \chi_A = 6211 \times 10^{-6}; \mu_s = 3.88.$$

7. *Ammonium nickel molybdate* was prepared by boiling a solution of ammonium paramolybdate with nickel sulphate. On cooling the green solution, light green crystals of the substance separated (cf. Rosenheim, *loc. cit.*). [Found: NH₃, 5.78; Ni, 4.97; MoO₃, 73.20; H₂O (from the loss by ignition and ammonia), 11.66. 3(NH₄)₂O, NiO, 6MoO₃, 7.5H₂O requires NH₃, 5.77; Ni, 4.97; MoO₃, 73.21; H₂O, 11.63 per cent].

$$t = 30^\circ; \chi_g = 3.49 \times 10^{-6}; \chi_u = 4109 \times 10^{-6}; \chi_A = 4223 \times 10^{-6}; \mu_s = 3.21.$$

8. *Ammonium cupric molybdate* was obtained as bluish white microscopic crystals from a cold solution of copper sulphate and ammonium paramolybdate (cf. Rosenheim, *loc. cit.*). [Found: NH₃, 5.62; Cu, 5.30; MoO₃, 71.66; H₂O (from the difference of loss by ignition and ammonia), 13.20. 2(NH₄)₂O, CuO, 6MoO₃, 6H₂O requires NH₃, 5.62, Cu, 5.24; MoO₃, 71.47 H₂O, 13.36 per cent].

$$t = 30^\circ; \chi_g = 1.30 \times 10^{-6}; \chi_u = 1506 \times 10^{-6}; \chi_A = 1602 \times 10^{-6}; \mu_s = 1.98.$$

9. *Ammonium manganous molybdate* was obtained from an acid solution of manganous chloride (10 g.) and a saturated solution of ammonium paramolybdate (24 g.) in the form of fine red, silky crystals, which turned yellow after some days. [Found: NH₃, 4.35; Mn, 4.65; MoO₃, 73.70; H₂O (by diff.), 13.61. 1.5(NH₄)₂O, MnO, 6MoO₃, 9H₂O requires NH₃, 4.34; Mn, 4.65; MoO₃, 73.53; H₂O, 13.79 per cent].

$$t = 25^\circ; \chi_g = 17.36 \times 10^{-6}; \chi_u = 20398 \times 10^{-6}; \chi_A = 20500 \times 10^{-6}; \mu_s = 7.0.$$

10. *Ammonium cobaltous molybdate* was prepared from a cold concentrated solution of cobalt chloride (10 g.) and a cold saturated solution of ammonium paramolybdate. Light violet, microscopic crystals separated after a few days (Rosenheim, *loc. cit.*). [Found: NH₃, 4.20; Co, 6.45; MoO₃, 74.11; H₂O (by difference), 13.04. 1.5(NH₄)₂O, CoO, 6MoO₃, 8.5H₂O requires NH₃, 4.36, Co, 6.41; MoO₃, 73.85; H₂O, 13.07 per cent].

$$t = 27^\circ; \chi_g = 11.07 \times 10^{-6}; \chi_u = 12940 \times 10^{-6}; \chi_A = 13040 \times 10^{-6}; \mu_s = 5.60.$$

11. *Sodium Mangan^{IV}-paratungstate*.—Manganese chloride (MnCl₂·6H₂O, 1g.) and sodium paratungstate (10 g.) were dissolved in 50 c.c. of water and the mixture was heated to boiling. To this 4g. of sodium persulphate were added in small portions at a time to oxidise the mixture. It was then filtered from the insoluble residue of manganese dioxide. The dark red filtrate, on standing for some days, deposited fine prismatic needle-shaped crystals of deep red colour. These were purified by recrystallization from hot water (cf. Just, *Ber.*, 1903, 36, 3619). [Found: Na, 7.75; Mn,

3.16 ; WO_3 , 66.45 ; O(active), 0.90 ; H_2O (by diff.), 18.25. $3\text{Na}_2\text{O}$, MnO_2 , 5WO_3 , $18\text{H}_2\text{O}$ requires Na, 7.86 ; Mn, 3.13 ; WO_3 , 66.06 ; O(active), 0.91 ; H_2O , 18.44 per cent].

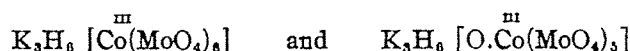
$t = 31.5^\circ$; $\chi_g = 2.96 \times 10^{-6}$; $\chi_m = 5205 \times 10^{-6}$; $\chi_a = 53.2 \times 10^{-6}$; $\mu_n = 3.58$.

In making the diamagnetic correction, χ_g for MoO_3 was taken as $+0.0975 \times 10^{-6}$ at 31° , as determined in our laboratory; for, the values given by previous workers differ widely from one another. For WO_3 , χ_g value of 0.2×10^{-6} , given by Barkmann and Zocher (*Z. physikal. Chem.*, 1926, **124**, 318) for 15° , was used.

DISCUSSION

The two compounds, ammonium and barium nickel molybdate with quadrivalent nickel, are practically diamagnetic. The ammonium compound shows very slight paramagnetism, due possibly to the presence of some accidental impurities or slight decomposition. A quadrivalent nickel ion with six electrons in the $3d$ -level should show a strong paramagnetic moment corresponding to four unbalanced electrons, *i.e.*, equal to about 5 Bohr magnetons from the Bose-Stoner's formula, $\mu_n = \sqrt{4S(S+1)}$, assuming that the orbital moments are completely quenched. Their diamagnetic character directly suggests that in these compounds the quadrivalent nickel atom constitutes the centre of a penetration complex with d^2sp^3 hybrid octahedral bonds. These substances are therefore, represented as molecular compounds of complex 6-molybdenum and 12-molybdenum heteropolyacid salts, or as a new 9-molybdenum complex, of the penetration type (*vide supra*).

Potassium cobaltic molybdates, compounds 2 and 3, as well as the ammonium salt of type 3, show also diamagnetism or very weak paramagnetic properties after diamagnetic correction. Obviously, the latter might be due to a slight decomposition, the pure substances being probably diamagnetic. Hence, the compounds must contain the trivalent cobalt as the central atom of a penetration complex with d^3sp^3 octahedral bonds. They should, therefore, be represented as containing a 6- or 5-molybdenum heteropoly complex anion as shown below :

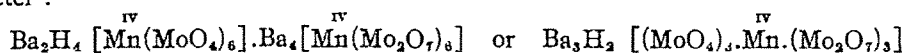


Ammonium chromic molybdate gives a magnetic moment of about 4 Bohr magnetons, which might be attributed to the free chromic ion, or to the trivalent chromium forming the central atom of an octahedral co-ordination complex of the penetration type with d^2sp^3 bonds. The colour and stability of the compound in aqueous solution, even at the boiling temperature, justify its inclusion in the 6-molybdenum heteropolyacid complex of the latter type.

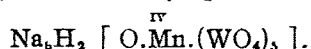
Ammonium ferric molybdate, on the other hand, shows a magnetic moment of 5.85 Bohr magnetons, characteristic of the ferric ion. Hence, the compound should be regarded as a 6-molybdenum heteropolyacid salt with the central ferric atom giving rise to a complex anion of the associated type with sp^3d^2 octahedral bonds, which might, therefore, resonate with ionic bonds.

Barium manganic molybdate shows a magnetic moment of 3.88 Bohr magnetons, which is to be expected for a quadrivalent manganese ion, as also for an associated or penetration type of complex with octahedral bonds. From a consideration of its

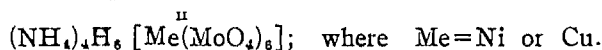
physical and chemical properties, and its resemblance to the corresponding quadrivalent nickel compound in composition, we may represent its constitution similar to that of the latter :



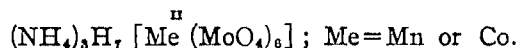
Similar result has been obtained also for sodium mangani-paratungstate with quadrivalent manganese. It gives a magnetic moment value of 3.58 Bohr. It, therefore, contains a complex heteropolyacid anion, represented by the following formula,



Ammonium nickel^{II} and cupric molybdate give magnetic moments of 3.2 and 1.98 Bohr magnetons respectively. This is characteristic of bivalent nickel and copper ions. These two compounds, therefore, belong to the 6-molybdenum heteropolyacid complex of the associated type :



Magnetic moment values for ammonium manganous molybdate and ammonium cobaltous molybdate, which are 7 and 5.6 Bohr respectively, agree more or less with those for the bivalent manganese and cobalt ions. The moment value found for the manganese complex is rather unusually high, being 7 in place of 5.8 to 6.0 found for the simple manganous salts. This makes the purity of the product, or the accuracy of the measurement of its moment value, rather doubtful. The matter, therefore, deserves a fresh examination. Nevertheless, the results indicate that both the compounds belong to the 6-molybdenum heteropolyacid complex of the associated type, resonating with that of the ionic one :



Thus the determination of the magnetic properties of this interesting class of compounds furnishes confirmatory evidence in support of Rosenheim's view about their constitution, which represents them as salts of heteropoly molybdic (tungstic) acid with the metal atom forming the centre of the co-ordinated complex. They can be further distinguished into complexes of the penetration and associated type, as revealed by their magnetic and chemical properties.

SUPERSATURATION COEFFICIENT AND THE PARTICLE SIZE OF THE SOLUTE

By B. S. SRIKANTAN

In a previous note (*this journal*, 1945, 22, 45), it has been shown that the supersaturation coefficient is inversely proportional to the size of the particles with which that solution is in equilibrium. Thus, for all values of r , which make K/r less than unity we have,

$$\frac{S-S_n}{S_n} = K/r \quad \dots (1)$$

The value of K being constant is given by $2M\sigma/RTd$ (where the terms have the same significance as mentioned before).

A concrete example shows that the value of K is such that it verges on the dimensions of a colloidal particle. In the case of gypsum ($d=2.32$, $\sigma=1050$ ergs per unit area at 25° , $M=136$; Hulett, *Z. physikal. Chem.*, 1901, 37, 385) $r=4.93 \times 10^{-6}$ cm. or about $50\mu\mu$. When, however, r grows smaller and verges on the threshold of "colloidal solutions", the linear relationship of equation (1) no longer holds and one may calculate only the approximate supersaturation coefficient in the different regions.

Particle size.	Approx supersat. coeff.
50 $\mu\mu$ to 25 $\mu\mu$	1.7 to 6.4
25 $\mu\mu$ to 10 $\mu\mu$	6.4 to 147
10 $\mu\mu$ to 5 $\mu\mu$	22025

When r grows still smaller one leaves the field of colloids and enters practically that of molecules.

It would be interesting to recall here that Von Weimarn ("Grundzuge der Dispersoid Chemie", 1911) in an investigation of the conditions of precipitation of slightly soluble substances arrived at the equation

$$\delta = \frac{c}{s} \cdot \eta \quad \dots (2)$$

where c is the potential solubility of the sparingly soluble substance, s , its normal solubility and η , the viscosity of the medium and δ , the degree of dispersion of the precipitate formed. The term c/s measures the supersaturation coefficient and is an inverse measure of the particle size (r). It is quite easy to show that conditions for precipitation of micro-particles are similar to those which prevail when the finer particles in a colloidal state come together and begin to precipitate, if one allows for the viscosity of the solution. In other words, Von Weimarn's equation leads to the same conclusion as in equation (1) until colloidal dimensions are approached.

The viscosity factor in equation (1) is included in the constant K

$$K = \frac{2M\sigma}{RTd} = \frac{2V_1\sigma}{PV} \quad \dots (3)$$

where P is the osmotic pressure, V , the volume of the solution and V_1 , the volume of the solute particles.

In the region of colloidal solutions (Einstein, *Ann. Physik*, 1906, **19**, 289)

$$\frac{V}{V_1} = \frac{\eta_s - \eta_o}{K_1 \eta_o}$$

where η_o is the viscosity of the dispersion medium and η_s is that of the disperse system ; K_1 is a constant.

Substituting in (1)

$$\frac{\tau(S - S_\infty)}{S_\infty} \left(\frac{\eta_o}{\eta_s - \eta_o} \right) = \frac{K_2 \sigma}{P}$$

where K_2 is constant.

This equation is a more complete representation of the factors involved than that given by equation (2) and has dimensions.

DEPARTMENT OF TECHNICAL CHEMISTRY,
COLLEGE OF ENGINEERING, GUINDY, MADRAS.

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STUDIES ON GUM JEOL (*ODINA WODIER*, ROXB.). PART I.

SOLUTION AND PURIFICATION

BY S. N. MUKHERJEE AND GOBINDALAL BANERJEE

Different samples of gum jeol, both old and freshly collected, have been tested for their miscibility with water and a method of purification for the same has been worked out by precipitation with alcohol. Freshly collected samples have been found to be readily miscible with water. Immiscibility with water is attributed not so much to the state of dehydration of the older samples as much to their age.

The gum is an indigenous product in many parts of India and is obtained as an exudate from plants commonly known in Bengal as Jeol trees (*Odina wodier*, Roxb.). Practically no work on this gum is to be found in the literature excepting the little recorded by Watt ("Dictionary of Economic Products of India"). This gum is used in many parts of India as a nutritive food specially after the puerperal period of women. The growing importance of the gum in commerce and industry justifies a thorough investigation into its physical and chemical behaviours. The present series of work embodies the results of such investigations. Work on the solution and purification of the gum has been taken up in this part to guide selection of samples, method of solution and purification and other conditions of experimentation.

The following samples of crude gum jeol were procured for examination. The samples were mostly collected from plants in October after the rains were over.

Sample 1. A freshly exuded semi-solid mass of brown colour, almost jelly-like in appearance, directly from plants.

Sample 2. A deep brown, old, air-dried sample, collected from the plant in the previous year after rains and preserved in a bottle.

Sample 3. A deep brown solid directly from the plant, collected in December.

Sample 4. Similar to sample 3.

Sample 5. A fresh semi-solid, brownish black sample, collected in October from a different locality.

Sample 6. An old, grey, powdery mass, purchased from the local market.

EXPERIMENTAL

All the samples contained considerable amounts of impurities which usually consisted of bark and leaves of plants, in some cases earthy matter and in one instance, probably some putrefied gum. These foreign matters were fortunately found to be insoluble in water and alcohol, the latter being the common precipitant for purification of the gum. An approximate but comparative estimate of the non-volatile impurities present was made by determination of the ash contents in the crude specimens, mentioned above (Table I) and

comparing these with the ash contents of some of the purified samples (Table II). The actual determination was made by slow incineration of known weights of the air-dried gum in platinum crucibles.

TABLE I

Sample No.	Weight taken.	Total ash obtained.	Ash%.	Mean value.
1*	6.12 g.	0.2754 g.	4.5	4.33%
	5.01	0.2015	4.2	
	4.10	0.1863	4.3	
2	4.20	0.1723	4.1	4.43
	4.51	0.2120	4.7	
	3.80	0.1712	4.5	
6	4.30	0.1375	3.20	3.26
	5.15	0.1572	3.02	
	3.19	0.1124	3.55	

Solution and Purification

Different samples of the crude gum were found not to go into solution in water easily. They thus offered a point of contrast with gum arabic (*Acacia arabica*) which would dissolve much more rapidly. Solubility of the different samples appeared to be different. The samples in the following discussion have been divided into three categories in each of which were noticed some peculiar features of interest.

Samples 1 and 5.—Both of them were brown, semi-solid, viscous masses freshly collected from the plants. Both of them were miscible with water in all proportions leaving the insoluble matters in gum as the only residue.

Purification of sample 1 was carried out according to the following procedure. About 5 g. of the crude gum were mixed with 15 c. c. of water (approx.), stirred well till the gum dissolved; and the solution filtered through filter paper. Filtration was slow and was interrupted by frequent choking of the filter papers which were therefore repeatedly renewed. Small amount of alcohol (2 c. c.) was then added to 10 c. c. of the filtrate, when a white viscous mass immediately came down, but on shaking this precipitate dissolved again. With addition of further amounts of alcohol (about 50% by volume) it was found that the precipitate no longer dissolved on shaking and the supernatant liquid suddenly became clearer. The precipitated mass, which was perfectly white and granular when first formed, gradually changed to a grey colour within a short time simultaneously settling to a sticky mass which could not be suspended again in the supernatant liquid. It has been observed as a matter of experience that when such a phenomenon occurs (the supernatant solution

* Sample 1 was, however, freed from moisture before incineration (as originally it was a semi-solid mass) by heating over a water-bath for 4 to 5 hours and keeping subsequently in a CaCl_2 -desiccator for 4 or 5 days till constant weight.

became clear and the precipitated gum sticky) this is an indication that the maximum amount of gum has precipitated out. The yield of the purified product after two such treatments with alcohol was about 60% as determined by separating the gum and carefully drying the same to a constant weight. The purified product was found to yield 2.7% of ash against 4.3% observed with the crude sample (Table II). Sample 5 also behaved similarly. The observations on both these samples appear in Table II.

TABLE II

Sample No.	Yield after twice precipitated with alcohol (approx.).	Ash content of samples	
		Purified.	Crude.
1	80%	2.7%	4.3%
5	55	3.1	5.5

Samples 3 and 4.—The samples were in the form of lumps. They were taken as such and mixed with 25 times their weight of double distilled water, previously sterilised by prolonged boiling and the mixture was preserved in bottles under toluene (pure, B. D. H.). The lumps did not readily mix with water but swelled more and more till the whole volume of the liquid was occupied. This took about 10 to 12 days' time for each sample. The solution had a brown colour and was transparent. Insoluble matters, mostly leaves, barks, etc., formed a compact scum on the surface which could be removed without any difficulty. This solution was dilute and it yielded about 5 to 6 g. of purified gum from about 50 g. of the crude sample in presence of approximately 80% of alcohol. A more concentrated solution (10 g. of gum in 100 c. c. water) could be prepared with these samples but a longer period of time (about 15-20 days) was necessary for the complete mixing of the gum with water. A dilute solution of the gum could, however, be concentrated by evaporation at ordinary temperature only under reduced pressure but not at high temperature, since the gum appears to be hydrolysed when the temperature is high (vide Part II of this series).

Samples 2 and 6.—Both of them were air-dried samples. About 25 g. of each sample, powdered in a mortar, were separately mixed with about 150 c. c. of water in two Jena bottles. The gums were found not to mix with water even by violent shaking with a mechanical stirrer for 10 to 12 hours. The major portion in both samples remained in a swollen state. The swollen mass and the dilute solution formed two distinct layers, the latter being on the top. The two layers did not mix even on keeping for two weeks. This evidently suggested that either the layers were in equilibrium or that the passage of one into the other was a very slow process. In the case of sample 2, it was observed that after a period of four months and a half the two layers disappeared and a homogeneous solution was formed. Sample 6 required longer time (about 6 months)

Both the layers (10 c. c.) in each sample were separately pipetted out and treated with absolute alcohol. It was observed that the upper layer in each case yielded no precipitate but only a slight turbidity even though the resulting concentration of alcohol was brought up to as much as 85%. The lower layer (swollen gum), however, yielded the precipitated gum in almost the original crude form having a thick brown colour when the concentration of alcohol was about 20%. It appeared that the phenomenon was due to the removal of water from the swollen gum by the added alcohol. No purified gum could, however, be obtained from these samples.

DISCUSSION

The different samples of the gum available for these investigations can thus be differentiated into three categories, as mentioned above, according to the age of the samples. The solubility behaviour differs in these three categories quite markedly. The greater the age of a sample, the lower is its solubility in water. Sample 2, which was known to be old and sample 6, which was obtained from the local market and whose age could not therefore be ascertained but which was undoubtedly very old as judged by its physical appearance, were the most insoluble among all the samples examined.

From the above observations at first it appeared that solubility depended on the loss of water on the part of the sample due to age and the drier a sample, the more insoluble it would be. This point was, however, further investigated by drying sample 1 on a thermostat slowly at 66°. This operation required about 7 days for completion. The solid thus obtained practically exhibited no difference in behaviour from the semi-solid parent body (sample 1) so far as its solubility was concerned. Age which was the only other alternative therefore appeared to be the determining factor in the difference in behaviour of the different samples. The yield of the purified product and the amount of alcohol necessary for its precipitation also appeared to depend on the age of the gum. If the sample be fresh and the concentration of the gum in solution be moderate (5-7%) then the concentration of alcohol necessary and sufficient for complete precipitation is about 50-60% and the yield is also about 60%. With moderately old samples concentration of alcohol found suitable for precipitation was about 70 to 80% and the yield 10% only. With very old samples two distinct layers appeared, one being a dilute solution which yielded almost no precipitate with alcohol. The second layer contained the swollen gum which precipitated readily with alcohol but did not yield pure products. The impurities were not eliminated.

Another observation in this connection was that in almost every case when the solution was not freshly prepared and/or the solution preserved for some time and then treated with alcohol, the precipitated gum was not sticky in the beginning but became sticky when kept in contact with the mother-liquor for a day or two.

CONCLUSIONS

To sum up the experience gathered in the preparation of a solution of this gum and its purification is that fresh samples obtained in the semi-solid state from the plant are the best to work with. When samples become dried up in air and become old they undergo marked decrease in solubility and the yield of the precipitated gum is also small. If the sample is fresh and soft, the purified gum obtained after precipitation by alcohol is fairly white in colour and the colour does not change easily. The aqueous solution from a white specimen of the purified gum is also colourless.

Soft and fresh samples of the gum, directly collected from a plant in the month of October after the rains were over (in Bengal), were therefore always used in the investigations recorded in subsequent parts of this series of study.

Our best thanks are due to Dr. J. N. Mukherjee, D. Sc., F. N. I., C. B. E., Director, Indian Agricultural Research Institute for his keen interest and valuable suggestions in connection with this work and to Dr. D. Chakravarti of the University College of Science for his kind co-operation.

PHYSICAL CHEMISTRY LABORATORIES,
COLLEGE OF ENGINEERING AND TECHNOLOGY, JADAVPUR
AND
UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA.

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STUDIES ON GUM JEOL (*ODINA WODIER*, ROXB.) PART II. HYDROLYSIS AND THE REDUCING SUGARS

BY S. N. MUKHERJEE AND GOBINDALAL BANERJEE

Gum jeol has been hydrolysed by H_2SO_4 (conc. $<0.5N$) to yield some reducing substances and a complex acid (termed *jeolic acid*) which forms colloidal solution in water. More drastic hydrolysis of the gum with H_2SO_4 (conc. $>1.5N$) by prolonged refluxing for 16 to 18 hours yields larger amounts of reducing substances, being about 86% (calculated as glucose) of the weight of the gum. These reducing substances have been identified and characterised as *l*-arabinose and *d*-galactose.

In Part I of this series of investigations (*J. Indian Chem. Soc.*, 1948, 25, 59) it has been observed that fresh gums, specially when collected in the semi-solid state, are readily miscible in water but, an old dry sample is only slightly miscible. This latter when kept in contact with water for a number of days gives a uniform solution. This naturally raises a question as to whether the gum in prolonged contact with water is changed by hydrolysis before passing into solution. In the present investigation an answer to this question has been attempted.

The second point investigated in this connection is the nature of the products, if the gum actually do hydrolyse in water. Gum arabic has been observed to yield (O'Sullivan, *J. Chem. Soc.*, 1884,45,41) on hydrolysis with H_2SO_4 , a pentose sugar (*l*-arabinose) and a relatively small amount of hexose (*d*-galactose) together with an acid which he termed the "arabic acid" and to which the molecules of arabinose and galactose were considered to be attached.

In the present investigation work on almost similar line has been pursued to isolate the hydrolysis products from gum jeol and to identify and characterise them. It has also been the object to indicate the approximate quantities of these products on the percentage basis.

EXPERIMENTAL

Gum jeol used in these experiments were purified by thrice precipitation by alcohol as recorded in Part I (*loc. cit.*).

Hydrolysis by Water.—Hydrolysis of the gum in aqueous solution on keeping was first examined. Appearance of reducing substances as products of hydrolysis was not, however, tested by Fehling's solution as the latter introduced alkali which itself might have hydrolysing effect. The hydrolysis was therefore followed by noting the change in optical rotation. The gum solution itself was observed to possess an optical activity, its specific rotation amounting to about $[\alpha]_D^{30} = +29^\circ$ (observed in 1% aqueous solution).

Aqueous solution in the cold showed no hydrolysis even when kept for a number of days. Clear evidence of hydrolysis began to appear roughly after a month's time. Warming the solution on a water-bath appeared to accelerate hydrolysis. This fact was corroborated by an examination with Fehling's solution when an immediate precipitation indicated previous hydrolysis. Fehling's solution added to the cold gum solution of the same concentration, as a control measure, failed to produce a distinct precipitate, but produced only a faint brown colour.

Hydrolysis of the gum in course of its purification by alcohol, as recorded in Part I (*loc. cit.*), was also examined by precipitation of the gum from a concentrated solution by alcohol and keeping the mixture as such for about 24 hours, after which the supernatant solution was tested with Fehling's solution. A slight but immediate precipitation confirmed previous hydrolysis. A gum solution, similarly preserved for over a month, also showed signs of hydrolysis. It was thus possible to find a clue to the solubility behaviour of some of the samples mentioned in Part I (*loc. cit.*) viz., samples 2, 3, and 4, which were found to be insoluble in the beginning but gradually went into solution when sufficient time was allowed.

Hydrolysis by Acids.—At the temperature of the water-bath vigorous and almost instantaneous reduction of Fehling's solution was noticed and a more copious precipitation, in comparison with a control in which no acid was added, confirmed the hydrolysing action of acids on this gum. A rough and qualitative

investigation revealed that perhaps hydrolysis was more vigorous with strong acids like HCl , H_2SO_4 , etc. than with weak ones (CH_3COOH , $\text{C}_6\text{H}_5\text{COOH}$).

Hydrolysis by Alkalis.—Alkaline hydrolysis was tested in a similar manner against a control in which no alkali was added. Copious and instantaneous precipitation in a gum solution (0.3%), warmed with an equal volume of $N/5\text{-NaOH}$ till the colour turned black, showed the presence of fairly strong hydrolysis in presence of alkalis.

Products of Hydrolysis

(a) *Mild Hydrolysis.*—To a clear 2% solution of the gum sufficient H_2SO_4 was added to make its concentration $0.5N$ and the mixture warmed on a water-bath for 2 hours. From the cooled solution H_2SO_4 was quantitatively removed by addition of $\text{Ba}(\text{OH})_2$ and filtration. The filtrate was made up to 250 c.c. from which an aliquot part was titrated by Fehling's solution, standardised by standard glucose solution with methylene blue as an indicator. The amount of the reducing substances is expressed in terms of percentage of glucose. Results are represented in the table below.

TABLE I

Gum sample.	Amount of gum taken.	Sugar expressed as glucose	Mean.
Sample 3*	40 g.	12.01 g.	30% 30% (approx.)
Sample 4*	36	10.70	29

Gum arabic with similar treatment yielded about 4 to 5% of reducing sugars (calc. as glucose; error $\pm 1.5\%$). Like gum arabic which on hydrolysis with $0.5N\text{-H}_2\text{SO}_4$ yields the arabic acid (cf. Sullivan, *loc. cit.*, also Thomas and Murray, *J. Phys. Chem.*, 1928, 32, 676; Pauli and Palmrich, *Kolloid Z.*, 1937, 79, 63), the gum jeol has been observed to yield besides the reducing substances an acid which will be subsequently referred to as "Jeolic acid" throughout these investigations. The hydrolysis carried out with $0.5N\text{-H}_2\text{SO}_4$ will be similarly referred to as the *mild hydrolysis*.

The jeolic acid, thus obtained, is quite a stable compound which is always obtained whatever be the method of mild hydrolysis, followed either by prolonged heating with acids or by electrodialysis with acids†.

The jeolic acid solution thus obtained formed a colloidal solution and it was freed from the sugars by dialysis after which the acid was obtained in the solid state by precipitation with alcohol (yield 10g. from 100g. of gum). The residue was dried on a water-bath to constant weight. A known weight of this acid was then dissolved in water.

(b) *Hydrolysis of the Jeolic Acid.*—Attempts were next made to estimate the amounts of reducing substances by a complete hydrolysis of the jeolic

* (Vide Part I).

† The procedure and the result of electrodialysis will be taken up in a future communication of this series.

acid by prolonged refluxing with H_2SO_4 (conc. $>1N$). Refluxing was continued for 16 to 18 hours (cf. Heidelberger and Goebel, *J. Exp. Med.*, 1929, 49, 459). From an analogy with gum arabic it was expected that such hydrolysis would yield some reducing sugars and a hexuronic acid which is usually known to form an insoluble barium salt. The excess of H_2SO_4 and all the hexuronic acid formed were quantitatively removed by the addition of BaCO_3 at the temperature of the water-bath till the solution was neutral to litmus paper. Precipitation was completed by keeping the solution overnight, after which Ba salts were filtered off and washed thoroughly with double distilled water till free from sugars. The filtrate and the wash liquid were cooled and mixed together when the mixture presented a yellow colour. A small portion of this yellow solution was tested with dilute H_2SO_4 for any barium uronate that might have escaped precipitation. A very faint turbidity roughly indicated a practical absence of such a salt in the solution. The solution was then made up to 500 c.c., an aliquot part of which was evaporated on a water-bath when a sticky, brown substance resembling molasses in appearance and odour suggested the presence of sugars. The amount of these sugars was determined by titration with Fehling's solution. The percentage of sugars in the jeolic acid was estimated to be 82%, 84.2% and 83% in three determinations yielding a mean value of 83.06. For the sake of comparison the arabic acid from gum arabic, which was also similarly treated, yielded sugar to the extent of 82.5%.

(c) *Total Reducing Sugars*.—From the above two stages of hydrolysis the total amount of reducing sugars in the two stages amounted to about 88.1% (expressed as glucose) of the air-dried, purified sample of gum jeol. With arabic acid the corresponding percentage was 62.1%. This figure for gum jeol was further confirmed by a direct drastic hydrolysis of a known weight of the gum with H_2SO_4 (conc. $>1.5N$) and estimation by Fehling's solution after removal of the excess of H_2SO_4 and all of the uronic acid by BaCO_3 . Two samples of purified gum jeol yielded the following results:

(i) Gum jeol (10 g.) yielded 3.5 g. of reducing sugars (calc. as glucose), 85%.

(ii) Gum jeol (7g.) yielded 6 g. of reducing sugars (as glucose), 86%

Gum jeol thus yields much greater amounts of reducing sugars than gum arabic.

Nature of the Reducing Sugars

For examination of the products of hydrolysis it was necessary to get the substance in as much pure a state as possible. For this reason the following procedure was adopted.

Crude gum (40 g.) was dissolved in 500 c.c. of 40% H_2SO_4 solution and heated on a water-bath for 2 hours. The solution was then neutralised by CaCO_3 . The precipitate formed was filtered off and washed several times with warm water. The washings were then transferred to the filtrate which

was then concentrated to 100 c.c. under reduced pressure. Alcohol (200 c.c.) was then added when the calcium salt of the complex jeolic acid (also of aldobionic and uronic acids, if formed) separated out as a white precipitate which was filtered off. The solution was next freed from alcohol under reduced pressure to a syrupy liquid of light red colour. A part of this solution was warmed on a water-bath with resorcinol and HCl when the appearance of a red colour indicated the presence of hexose.

Pentoses were similarly detected with the help of Tollen's reagent when a red colour appeared in 2 to 3 minutes' time at the temperature of the water-bath. This was confirmed by the addition of FeCl_3 solution when the colour changed from red to green. The orcinol test was not, however, characteristic of pentoses alone but of uronic acids as well, but since uronic acid had been eliminated by formation of its Ca salt and precipitation by alcohol, the response to the test might be due to the presence of pentose alone in this case.

Characterisation of the Pentose.—A part of the syrupy mother liquid, mixed with twice its volume of methyl alcohol, was kept in the refrigerator at 0° for crystallisation. A faint turbidity appeared in about 12 hours' time. On addition of some more methyl alcohol crystals appeared in about 24 hours' time and after about 2 hours the crystallisation appeared to be complete. The good crop of crystals, thus obtained, was separated by filtration; the yield was about 0.7 g. from about 15 g. of sugar mixture, concentrated by evaporation of the mother-liquor in *vacuo* and drying at room temperature in a vacuum desiccator. The crystals were then recrystallised from methyl alcohol, m.p. was 151° at first, but was it raised to 153° and then to 155° after four crystallisations (mixed m.p. with Merck's *L*-arabinose, 154°). Specific rotation $[\alpha]_D^{25} = +105^\circ$. Hence the product appears to be pure *L*-arabinose. It was further confirmed by converting the sugar into its osazone, m.p. 148-50°, while the m.p. of the corresponding compound of *L*-arabinose is 157°. The combustion analysis of the substance shows C, 40.1; H, 6.72; O, 53.2% (*L*-arabinose gives C, 40.0; H, 6.67; O, 53.3%). It is therefore justifiable to conclude that the sugar separated by the above procedure, and purified by repeated crystallisations from methyl alcohol is probably *L*-arabinose but the phenylosazone might be a mixture of osazone and phenylhydrazone.

Characterisation of the Hexose.—A portion of the solution obtained after separating the crystals in the above procedure was carefully evaporated to dryness under reduced pressure and the sugar present in solution recovered in the dry state by desiccation in a vacuum desiccator. This was then dissolved in minimum amount of water and treated with methyl alcohol to get rid of the pentose that might still be present. After repeating this process thrice the sugar was obtained in the dry state by evaporation and tested for its specific rotation; $[\alpha]_D^{25} = +78.5^\circ$ (observed in 1% aqueous solution).

A small quantity of sugar was dissolved in minimum amount of water and oxidised with 1:1 nitric acid by heating on a water-bath for about $\frac{1}{2}$ hour. The solution was then rapidly cooled under the tap and vigorously scratched, when fine crystals began to appear. On keeping this solution overnight further amounts of the crystals appeared, but on keeping for 4 days sufficient quantities could be collected. The crystals were needle-shaped, m.p. $214-16^{\circ}$. This compares favourably with the m.p. of mucic acid (218°). The substance was insoluble in cold water and alcohol but dissolved sparingly in boiling water from which it was purified by crystallisation. It was, however, insoluble in boiling alcohol. The aqueous solution was strongly acidic to litmus. All these properties suggest the substance to be mucic acid. It was further confirmed by converting it into its tetraacetyl derivative, m.p. 262° ; the crystals are insoluble in water but readily soluble in alcohol. The melting point agrees well with that of the tetraacetyl derivative of mucic acid (m.p. 266°). This strongly indicates the presence of hexose in this case as *d*-galactose, which was finally confirmed by noting the mixed m.p. with Merck's *d*-galactose (217° sharp) (m.p. of the purified substance has been observed to be $214-216^{\circ}$ and that of Merck's *d*-galactose, 218°).

The mother-liquor after separation of the hexose was further tested for any reducing substances that might still be left, but no such indication was obtained. Hence, the reducing substances are the two types of sugars only, viz., pentose (*L*-arabinose) and hexose (*d*-galactose). A rough estimation of the pentose by furfural reaction and of the hexose by subtracting the amount of pentose from the total amount of reducing sugars estimated by Fehling's solution shows the ratio of pentose to hexose as 1 : 1.3.

CONCLUSIONS

Both gum arabic and gum jeol yield on hydrolysis sufficient quantities of reducing sugars which are mainly *L*-arabinose and *d*-galactose. The facts that gum jeol yields about 86% of its weight of reducing sugars as compared to about 62% in the case of gum arabic on drastic hydrolysis, and that gum jeol in aqueous solution hydrolyses spontaneously show that the latter is a more complex body. But whether the difference in properties of the two gums can be attributed to the difference in their sugar contents alone will be taken up for discussion in a subsequent communication.

Our thanks are due to Dr. J. N. Mukherjee, D.Sc., F.N.I., C.B.E., Director, Indian Agricultural Research Institute, New Delhi for his keen interest and helpful suggestions and to Dr. D. Chakravarti of the University College of Science for his valuable help in connection with combustion analysis.

PHYSICAL CHEMISTRY LABORATORIES,
COLLEGE OF ENGINEERING AND TECHNOLOGY, JADAVPUR,
AND UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA.

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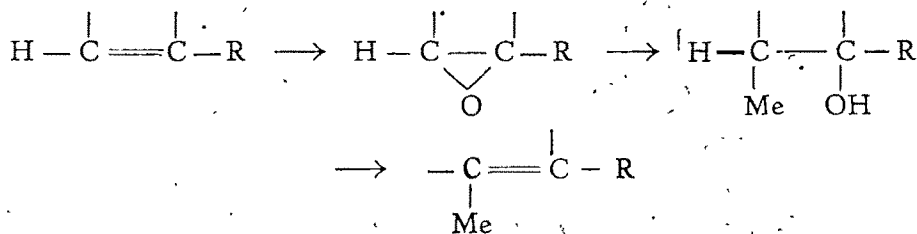
STUDIES IN SESQUITERPENES. PART II.
SYNTHESES OF METHYLCADALENES

B'Y SUKH DE'V

5-Methyl-, 8-methyl- and 3-methyl-cadalenes have been synthesised.

In connection with our investigations on the sesquiterpenes of the cadinene group it became necessary to ascertain the properties of all the five possible methylcadalenes, and 1-methyl-6-ethyl-4-*isopropyl*-, and 1-ethyl-6-methyl-4-*isopropyl*naphthalene. Of the five methylcadalenes, 2-methyl- and 7-methylcadalene have been prepared previously by Campbell and Soffer (*J. Amer. Chem. Soc.*, 1942, 64, 417), the syntheses of the remaining three are reported in this paper.

The necessity for the preparation of these compounds arose in connection with the location of the double bonds of a new bicyclic sesquiterpene (cadinene group). The method is similar to that employed by Ruzicka and Sternbach (*Helv. Chim. Acta*, 1940, **23**, 124) for the location of the nuclear double bond of *dextro*-pimaric acid. The method has also been used by Campbell and Soffer (*loc. cit.*) in revising the structure of cadinene. A mono-oxide, prepared by the action of one mole of perbenzoic acid (or percamphoric or perphthalic acid) on one mole of the sesquiterpene (here, the word sesquiterpene will refer to a sesquiterpene of the cadinene group), will react with methyl magnesium iodide, introducing a methyl group in the molecule :

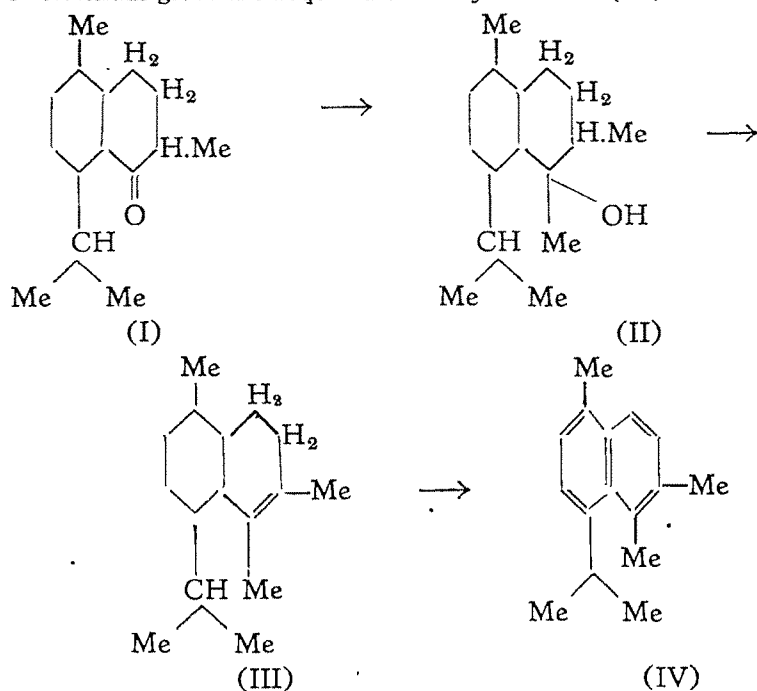


Thus, the position of the additional methyl group in the molecule will reveal the position of the ethylenic linkage.

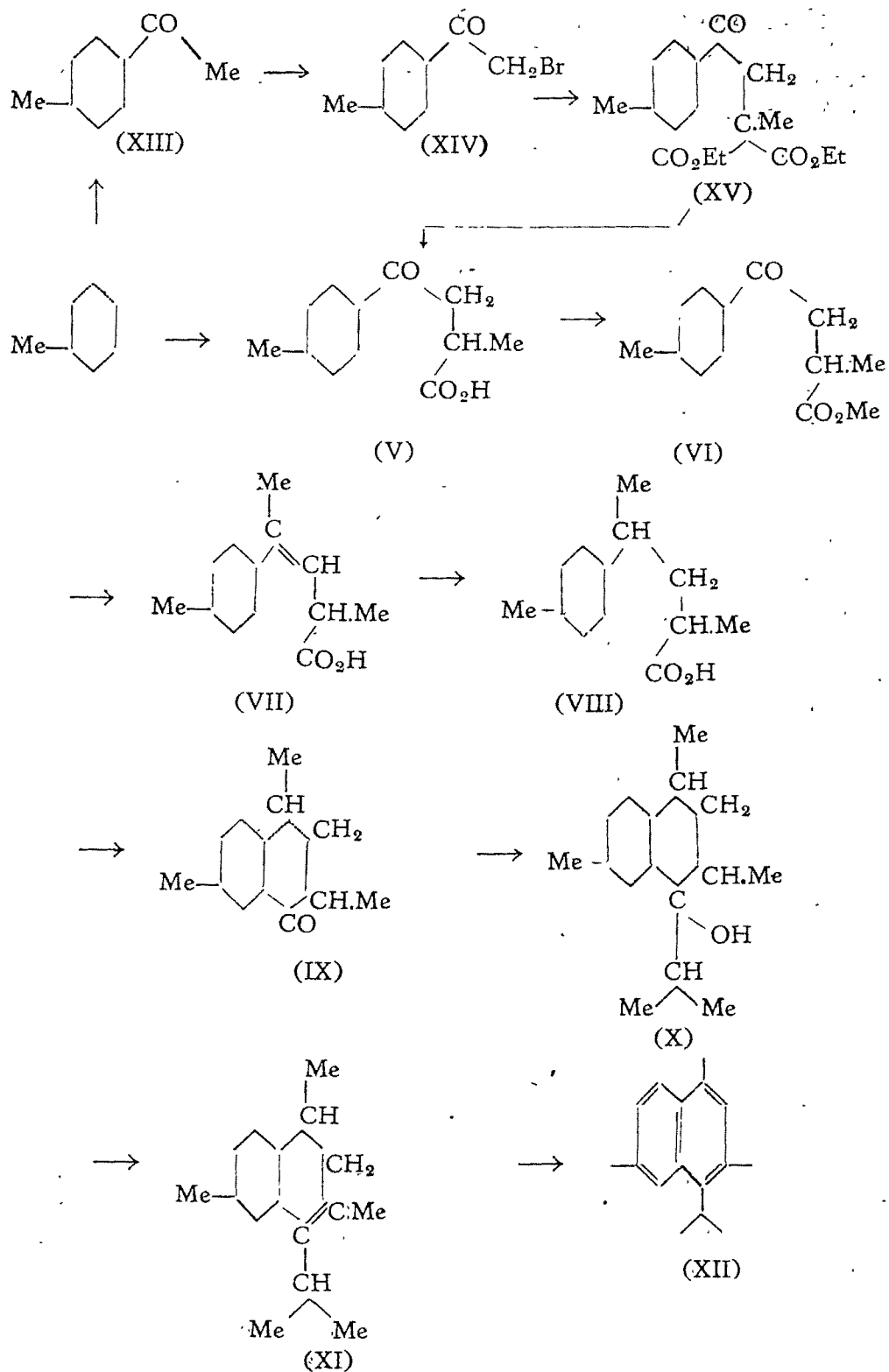
The method can be extended to include the ketones and the primary and secondary alcohols of this group. The position of a keto group in the molecule can be readily established by identifying the methylcadalene produced by the dehydrogenation of the tertiary carbinol obtained by the reaction of magnesium methyl iodide on the ketone. The method has been used by Bradfield and co-workers in fixing the position of the carbonyl group of tetrahydro-eremophilone, a sesquiterpene ketone of the eudalene group (*J. Chem. Soc.*, 1936, 667). The secondary alcohols can be oxidised to the corresponding ketones by the elegant method of Oppenauer (*Rec. trav. chim.*, 1937, 56, 137) and then the method used. Similarly, the aldehyde obtainable by the oxidation of a primary alcohol can be employed.

The application of these methods will be reported in future communications.

1 : 5 : 6-Trimethyl-4-isopropyl*naphthalene* (IV).—2 : 5-Dimethyl-8-*isopropyl*tetralone-1 (I), prepared from *p*-cymene (Sukh Dev and Guha, *J. Indian Chem. Soc.*, 1948, 25, 13), is treated with magnesium methyl iodide to give a mixture of the carbinol (II) and its dehydration product. The mixture is completely dehydrated with 90% formic acid giving 1 : 5 : 6-trimethyl-4-*isopropyl*-7 : 8-dihydronaphthalene (III). Dehydrogenation of this hydrocarbon by means of selenium gives the required 5-methylcadalene (IV).

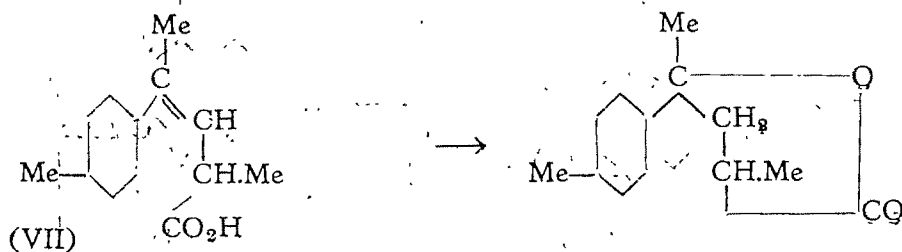


1 : 3 : 6-Trimethyl-4-isopropyl*naphthalene* (XII).—Toluene is condensed with methylsuccinic anhydride in nitrobenzene in the presence of anhydrous aluminium chloride to give β -(*p*-toluyl)- α -methylpropionic acid (V). This reaction has been previously reported by Mayer and Stamm (*Ber.*, 1923, 56, 1424). They carried out the reaction in excess of toluene as a solvent for 2 hours at room temperature and 2 hours on the water-bath and obtained a 77% yield of the crude product, which consisted of a mixture of β -(*p*-toluyl)- α -methylpropionic acid (39.6%) and β -(*p*-toluyl)- β -methylpropionic acid (56.6%). However, by our procedure, β -(*p*-toluyl)- α -methylpropionic acid is the chief product and is obtained in an excellent yield of 80-86%. The melting point of our compound is 174-75°, whereas Mayer and Stamm have reported it as 169-71°. In view of this difference it became necessary to confirm the structure of our product. This has been done by synthesising this acid from 4-acetyl-toluene (XIII). This is brominated with one mole of bromine to give the ω -bromo compound (XIV). The latter is condensed with the sodium salt of



methylethylmalonate, giving the *isosuccinic* ester (XV), which is hydrolysed and decarboxylated to (V), m.p. 173-74° (mixed m. p. with the Friedel-Craft's product, 173.5-174.5°). This synthesis has also been reported by Mayer and Stamm (*loc. cit.*).

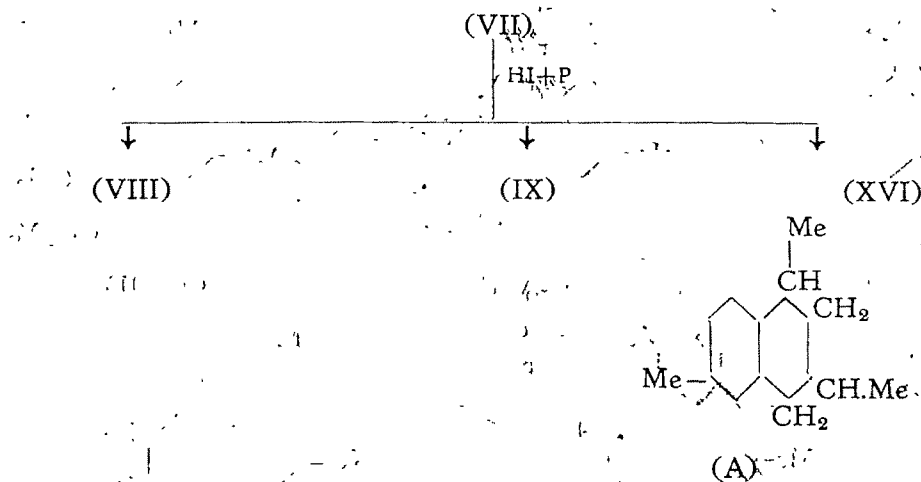
Next, the inverse Grignard's reaction of magnesium methyl iodide on methyl β -(*p*-toluyl)- α -methylpropionate (VI) was carried out. By following the details of a procedure recommended by Kloetzel for a similar reaction (*J. Amer. Chem. Soc.*, 1940, 62, 1708) we could only get yields of 50-60%. There are many variables in this reaction which can affect the yield. A systematic investigation reveals that the amount of the Grignard reagent, the time and the temperature at which the hydrolysis of the reaction complex is carried out, are the most important factors. By proper control of these variables, consistent yields of 90-95% of the crude material could be easily obtained. For one mole of the ester 1.7 moles of the Grignard reagent should be employed. The decomposition of the reaction complex should be carried out by adding dilute hydrochloric acid (1:1) to the reaction mixture, cooled to about 2°-5°, and then the whole thing should be worked up immediately after the complex is dissolved. If the reaction mixture is allowed to remain in contact with the mineral acid for a longer period, a considerable amount of the unsaturated acid produced is lost through lactonisation, the separation of which from any unreacted keto-ester is very difficult. The γ -(*p*-tolyl)- γ : α -dimethyl-vinylacetic acid (VII) is obtained as a viscous liquid, which does not crystallise.



The crude acid could not be purified by distillation, since in all cases the acid completely lactonised on distillation at 2 to 3 mm.

The catalytic reduction of (VII) with Adam's platinum oxide catalyst was not attempted, since the acid could not be easily purified. Reduction with Raney-nickel in alcohol at 80° and 70 lbs. pressure, could not be achieved. Hence the compound was submitted to reduction with hydriodic acid and red phosphorus. The reduced acid could only be obtained in 50% yield, while a considerable amount of the material is found in a neutral fraction. If the time of reaction be increased, the yield of the reduced acid falls and that of the neutral fraction rises. In one instance (40 hours' refluxing) the

neutral fraction was the chief product (70%). The neutral fraction can be easily separated by repeated fractionations into two compounds (A), b. p. 110-114°/4 mm. and (B), b. p. 135-40°/4 mm. Of these, (B) has been shown to be 2:4:7-trimethyltetralone-1 (IX), the m. p. of its 2:4-dinitrophenylhydrazone (m. p. 220.5-22.5°) remains undepressed on admixture with the

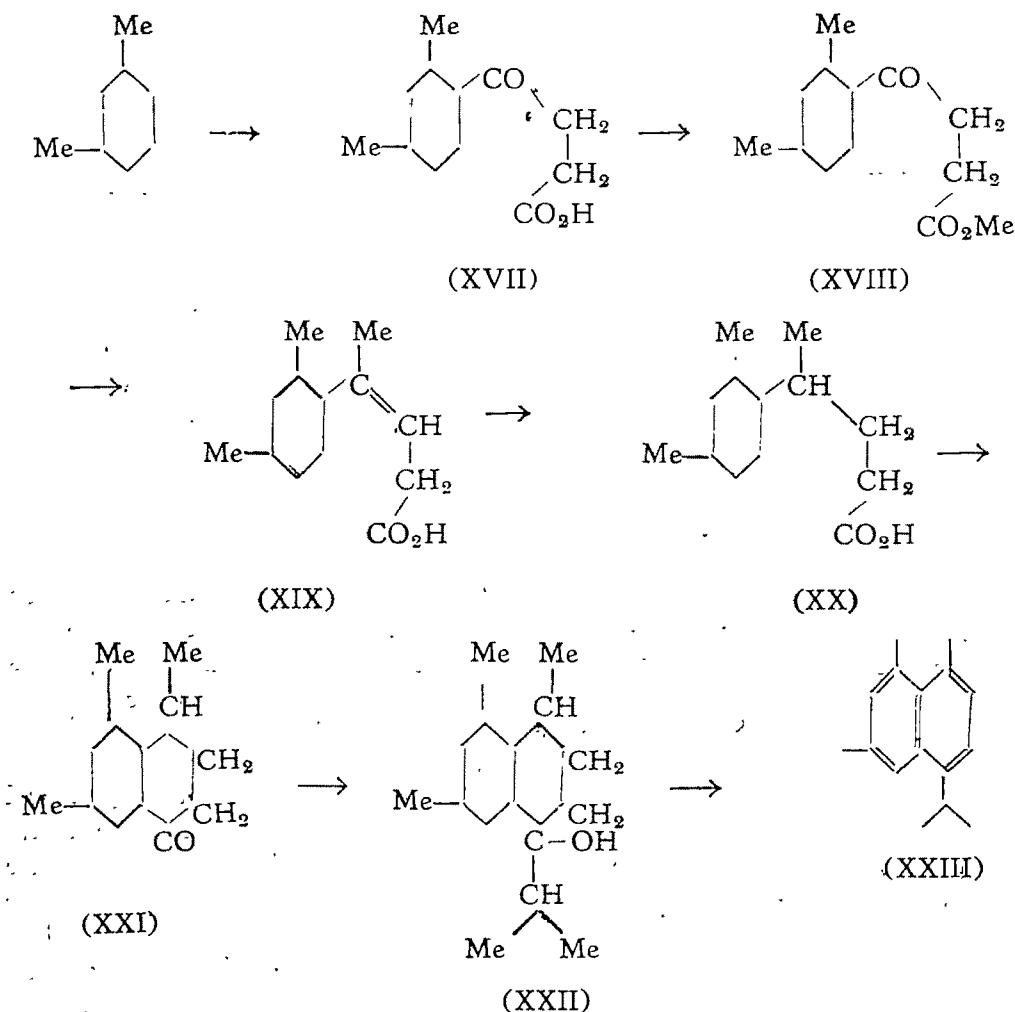


2:4-dinitrophenylhydrazone of (IX). The fraction (A) appears to be 1:3:6-trimethyl-1:2:3:4-tetrahydronaphthalene (XVI), a fact which has been confirmed by the dehydrogenation of the compound with sulphur, when 1:3:6-trimethylnaphthalene is isolated and identified as its picrate and styphnate. This part of the reaction is being studied further.

The intramolecular ring-closure of γ -(*p*-tolyl)- γ : α -dimethylbutyric acid (VIII) is readily effected by means of anhydrous aluminium chloride to give 2:4:7-trimethyltetralone-1 (IX). By the action of magnesium isopropyl bromide on the ketone, an unstable carbinol (X) is obtained which on dehydration with acetic anhydride gives 1:3:6-trimethyl-4-isopropyl-1:2-dihydronaphthalene (XI) from which 3-methylcadalene is obtained by dehydrogenation with selenium.

1:6:8-Trimethyl-4-isopropyl-naphthalene (XXIII).— β -(2-*m*-xyloyl)-propionic acid (XVII) has been prepared by the action of succinic anhydride on *m*-xylene in nitrobenzene solution in the presence of anhydrous aluminium chloride (cf. Barnett and Sanders, *J. Chem. Soc.*, 1933, 434). Its methyl ester (XVIII) on treatment with magnesium methyl iodide gives γ -(2-*m*-xylyl)- γ : α -methylvinylacetic acid (XIX). This unsaturated acid is also a liquid which could not be distilled unchanged owing to its readiness to lactonise on

distillation under reduced pressure. The acid is reduced with hydriodic acid and red phosphorus to yield γ -(2-*m*-xyl-yl)-valeric acid (XX). In this case also, a small neutral fraction is obtained, which contains the corresponding tetralone. This acid has been previously prepared by Heilbron and Wilkinson from 2 : 4-dimethylacetophenone (involving 8 steps) (*J. Chem. Soc.*, 1930, 2538).



But the present method is much simpler (4 steps) and the yields are very good. The acid is cyclised by anhydrous aluminium chloride to give 4 : 5 : 7-trimethyltetralone-1. (XXI). The ketone is treated with magnesium isopropyl bromide when an unstable carbinol (XXII) is obtained, the latter is dehydrated with 90% formic acid and then dehydrogenated with sulphur to yield 8-methylcadalene (XXIII).

All the methylcadalenes, thus synthesised, have been characterised by the preparation of suitable derivatives. By far the best reagent for the characterisation of these hydrocarbons appears to be trinitrobenzene. Its molecular compounds are very stable, sparingly soluble in alcohol, and can be easily obtained pure by a single crystallisation from 80% acetic acid. The reagent is recommended for the characterisation of all the methylnaphthalenes.

The melting points of the derivatives of all the five methylcadalenes are tabulated below :

Methylcadalene.	Picrate. m.p.	Styphnate. m.p.	T N B. compound. m.p.	T. N T. compound. m.p.
2-Methyl-*	143-44°	170-71°	168-69°	—
3-Methyl-	162-63°	—	165°	—
5-Methyl-	102.5-103.6°	130-31°	160-61°	87-8°
7-Methyl-*	122-23°	—	—	—
8-Methyl-	108-8.5°	—	118-18.5°	—

* Campbell and Soffer, *loc. cit*

Work on the syntheses of 1-methyl-6-ethyl-4-*isopropyl*- and 1-ethyl-6-methyl-4-*isopropyl*-naphthalene is in progress.

EXPERIMENTAL

1 : 5 : 6-Trimethyl-4-*isopropyl*naphthalene (IV)

1 : 5 : 6-Trimethyl-4-*isopropyl*-7 : 8-dihydronaphthalene (III).—A solution of 2 : 5-dimethyl-8-*isopropyl*tetralone-1 (I, prepared from *p*-cymene according to the method of Sukh Dev and Guha, *loc. cit.*) (10.0 g., 1 mol.) in dry ether (40 c.c.) was added gradually from a dropping funnel with continuous swirling to a well cooled (ice and salt) solution of magnesium methyl iodide (Mg, 1.6 g., 1.25 mol.; MeI, 10 g., 1.5 mol. and anhydrous ether, 50 c.c.). The mixture was left in the ice-bath for 15 minutes and then allowed to attain the room temperature (32°). The reaction went on quite vigorously at room temperature for half an hour, when a white solid separated. The reaction was completed by refluxing for 5 hours and the product decomposed by adding on to ice and ammonium chloride. The ether layer was separated, washed with a saturated solution of ammonium chloride and dried over anhydrous sodium sulphate. On removing the ether, a slightly reddish yellow viscous oil consisting chiefly of the carbinol was left. This was completely dehydrated by warming it with 90% formic acid (20 c.c.) on the water-bath for 2½ hours. 1 : 5 : 6-Trimethyl-4-*isopropyl*-7 : 8-dihydronaphthalene was isolated in the usual manner and purified by distillation over sodium as a colourless, mobile liquid, b.p. 140-43°/2.5 mm., yield 9.0 g. (90%).

1 : 5 : 6-*Trimethyl-4-isopropyl-naphthalene* (IV).—The above dihydromethylcadalene (9.0 g.) and selenium (4.5 g.) were heated together for 1 hour at 280° and then at 300°-310° for 24 hours and finally at 320° for 4 hours and then the product was worked up in the usual manner. The hydrocarbon (IV) was purified by several distillations over sodium as a colourless, mobile liquid, b.p. 132°/1.5 mm., yield 5.0 g. (56%). (Found : C, 90.12 ; H, 9.56. $C_{16}H_{20}$ requires C, 90.56 ; H, 9.43 per cent).

The *picrate*, prepared in the usual manner, was recrystallised thrice from alcohol as deep red needles, m.p. 102.5-103.5°.

The *styphnate*, prepared from styphnic acid (0.5 g.) and the hydrocarbon (0.5 g.) in 5 c. c. of alcohol, was recrystallised thrice. The pure compound separated from alcohol in orange needles, m. p. 130-31°.

Trinitrobenzene Compound.—Trinitrobenzene (0.5 g.) was dissolved in hot alcohol (20 c.c.) and the methylcadalene (0.5 g.) added. The mixture was heated till a clear solution was obtained, and then allowed to crystallise slowly. The crystals were filtered, washed with a small amount of cold 80% acetic acid and then with alcohol and dried. The product was recrystallised from 80% acetic acid (10 c.c.) as long, golden yellow needles, m.p. 160-61°. Further crystallisations did not raise the m.p.

Trinitrotoluene Compound.—T.N.T. (0.5 g.) was dissolved in hot 80% acetic acid (5 c.c.) and the hydrocarbon (0.5 g.) was added and the mixture heated till a clear solution was obtained ; it was allowed to cool slowly. The compound was removed by filtration and recrystallised twice from 80% acetic acid (3 to 5 c.c.) as deep yellow needles, m.p. 87-88°. The compound could not be crystallised easily from alcohol due to its dissociation in the solvent.

1 : 3 : 6-*Trimethyl-4-isopropyl-naphthalene* (XII)

β -(*p*-ToluyI)- α -methylpropionic Acid (V) : *Condensation of Methylsuccinic Anhydride with Toluene*.—Pyrotartaric anhydride (34.2 g., 1 mol.) was condensed with toluene (30.6 g., 1.1 mol.) in dry nitrobenzene (150 c.c.) in presence of anhydrous aluminium chloride (89.1 g., 2.12 mols.). The details as given for the preparation of β -(*p*-cymoyl)- α -methylpropionic acid (Sukh Dev and Guha, *loc. cit.*) were followed. Yield of the crude product (m.p. 160-62°) was quantitative. The product was crystallised from 90% acetic acid as colourless plates, m.p. 174°-75°, yield 53.0 g. (85.7%).

Synthesis of (V) from 4-Acetyl-toluene.—4-Acetyl-toluene (6.7 g., 1 mol.) in dry ether (10 c.c.) was brominated with bromine (8.0 g., 1 mol.) following the details given for the preparation of ω -bromoacetophenone ("Organic Synthesis", Vol. XIX, p. 24), yield 8.5 g. (80 %), m.p. 49°-50° (cf. Kunckell, *Ber.*, 1897, 30, 577, 1713).

4-Methyl- ω -bromoacetophenone (8.0 g., 1 mol.) was condensed with the sodium salt of methyldiethylmalonate (from sodium, 0.9 g. and ester, 6.5 g.)

in dry benzene (30. c.c.). The condensation was effected, and the *isosuccinic* ester hydrolysed and decarboxylated by following the details given for the preparation of β -(*p*-cymoyl)- α -methylpropionic acid (Sukh Dev and Guha, *loc. cit.*). The product crystallised from acetic acid (90%) in colourless plates, m.p. 173-74°, yield 4.0 g. (52%) (mixed m.p. with the Friedel-Craft's condensation product, 173.5-174.5°).

Methyl β -(p-Tolyl)- α -methylpropionate (VI).—Acid (45.0 g.), methanol (100 c.c.) and sulphuric acid (conc., 6.0 c.c.) were refluxed for 10 hours and worked up in the usual manner. The crude product was recrystallised from dilute alcohol as colourless, lustrous, long plates, m.p. 46°, yield 90-93%. (Found : C, 70.95 ; H, 7.54. $C_{13}H_{16}O_3$ requires C, 70.90 ; H, 7.27 per cent).

γ -(p-Tolyl)- γ : α -dimethylvinylacetic Acid (VII).—A Grignard solution of magnesium methyl iodide was prepared from magnesium (2.2 g., 1.7 mol.), MeI (15.0 g.) and dry ether. (25 c.c.). The ester (11.0 g., 1 mol.) was dissolved in dry ether (70 c.c.) and chilled in an ice-salt bath (-15°) to below 0° and the Grignard solution was added in a very thin stream with continuous swirling (20-30 mins.) Each drop reacted vigorously with the precipitation of a white solid. The reaction mixture was allowed to stand in the ice-bath with occasional swirling till it attained the room temperature (25°, 2 hours) and it was then refluxed on the water-bath for 3 hours ; it was finally allowed to stand overnight (12 hours). The white solid had by that time completely changed into a viscous semi-solid. The product was cooled in an ice-bath to about 5° and dilute HCl (1 : 1, 60 c.c.) was introduced in a thin stream from a dropping funnel with vigorous shaking (10 mins.). The complex should have decomposed by then, if not, the mixture should be thoroughly shaken to dissolve the complex. The reddish ether layer was then separated, washed once with water and extracted four times with dilute Na_2CO_3 solution. The extract was treated with norit and acidified with dilute hydrochloric acid (Congo red) and the liberated oil extracted with ether (thrice). The ethereal solution was dried over anhydrous magnesium sulphate and the solvent removed, when a slightly viscous reddish yellow oil was left, yield 9 to 9.5 g. (90-95%). The product was unsaturated to bromine in chloroform and was used as such in the next step.

γ -(p-Tolyl)- γ : α -dimethylbutyric Acid (VIII).—The above crude acid (18.0 g.) was reduced by refluxing for 16 hours with hydriodic acid (*d* 1.7, 100 g.) and red phosphorus (12.0 g.) at 130-140°. The reaction mixture was cooled, diluted with water and extracted with ether several times. The ethereal extract was washed with water twice and extracted with dilute sodium carbonate solution (4 times). The ether solution which contained the neutral products was kept apart for being treated later. The alkaline extract was clarified with norit and acidified with dilute hydrochloric acid (Congo red). The acid was extracted with ether (thrice) and the extract was washed with a sodium bisulphite solution to remove any iodine and then it was washed

with water and dried over anhydrous magnesium sulphate. The ether was distilled off and the crude acid left behind was purified by distillation as a colourless, viscous liquid, b. p. 176°/7.5 mm., yield 9.0 g. (50%). (Found : C, 75.99 ; H, 9.09. $C_{13}H_{18}O_2$ requires C, 75.72 ; H, 8.73 per cent) (cf Ruzicka and Ehmann, *Helv. Chim. Acta*, 1932, 15, 154).

The ethereal solution containing the neutral products was first washed with sodium bisulphite solution to remove the free iodine and it was then washed once with water, and dried. The ether was removed and the residue was twice fractionated carefully from a modified Claisen's flask. Two main fractions were obtained.

Fraction.	B.p.	Yield.	Remarks.
A	110-14°/4 mm.	2.0 g.	Colourless, mobile liquid
B	185-10°/4	4.0	Do

Fraction A.—It was once distilled over sodium. The hydrocarbon (1.5 g.) was dehydrogenated with sulphur (0.65 g.) at 230° for 30 minutes and then at 260° for 20 minutes. 1 : 3 : 6-*Trimethylnaphthalene* was isolated in the usual manner and purified by distillation over sodium as a colourless, mobile liquid, b.p. 115°-20°/3 mm., yield 75%.

The *picrate* was obtained as deep orange needles, (alc.), m.p. 114°-15° (Lit.* m.p. 115°). The *styphnate*, prepared in the usual manner, crystallised from alcohol in yellow, silky needles, m.p. 126° (Lit.* m.p. 126°. Ruzicka has given a m.p. of 148° at page 155, while in a table on page 142, he gives 126° as the melting point).

Fraction B.—This was identified to be 2 : 4 : 7-*trimethyltetralone*-1 (IX) by preparing the 2 : 4-dinitrophenylhydrazone, as a bright red, crystalline powder (benzene & petrol), m.p. 220.5-22.5° (mixed m.p. with an authentic sample remained undepressed).

2 : 4 : 7-*Trimethyltetralone*-1 (IX).— γ -(*p*-Tolyl)- γ : α -dimethylbutyric acid (15.0 g.) in dry benzene (30 c.c.) was converted into the acid chloride by phosphorus pentachloride (16.8 g. covered with 30 c.c. of dry benzene) in the usual manner and the acid chloride without being isolated was cyclised by anhydrous aluminium chloride (10.6 g.). The details as given for the cyclisation of γ -(*p*-cymyl-2)- α -methylbutyric acid (Sukh Dev and Guha, *loc. cit.*) were followed. The reaction was complete in 20 to 30 minutes. The product was obtained as a colourless, mobile liquid, b.p. 131°/3 mm., yield 80-88%. (Found : C, 82.88 ; H, 8.69. $C_{13}H_{16}O$ requires C, 82.97 ; H, 8.51 per cent).

The 2 : 4-dinitrophenylhydrazone crystallised from benzene-petrol mixture as a bright red crystalline powder, m.p. 220.5-22.5°.

1 : 3 : 6-*Trimethyl-4-isopropylnaphthalene* (XII).—A Grignard solution of magnesium isopropyl bromide was prepared from magnesium (3.1 g., 1.6 mol.),

* Ruzicka & Ehmann, *loc. cit.*

concentration decreased regularly from 0.2427 *M* to 0.2324 *M*. Therefore, the variation in relative viscosity could by no means be solely attributed to the increase in temperature. Further, no theoretical explanation was offered for the variation in relative viscosity with temperature both negative and positive. Whereas, in our previous paper an attempt was made to correlate the variation of relative viscosity with Rabinovich's solvate hypothesis and the depolymerisation hypothesis of Applebey (*this Journal*, 1948, 25, 39).

An attempt has been made to extend the above ideas to solutions of non-electrolytes in non-aqueous solvents in the present communication.

EXPERIMENTAL

Viscosity was measured in the same manner as was done by Chatterji and Gopal (*loc. cit.*), the modifications in the method adopted provided an arrangement for passing a current of dust-free air through the whole apparatus. The kinetic energy correction term, which is very small, has been neglected.

The results calculated from the viscosity data thus obtained are tabulated below.

TABLE I

Solvent.	Solute.	*Conc.	20°.	25°.	30°.	35°.	40°.	45°.	50°.
1. Hexane	Naphthaline	15.66	—	1.223	1.226	1.218	1.221	1.218	—
		25.50	—	1.321	1.325	1.319	1.316	1.310	—
2. „	Diphenylamine	9.83	—	1.258	1.241	1.241	1.228	1.214	—
		33.32	—	—	1.717	1.682	1.650	1.610	—
3. Benzene	Naphthaline	54.00	—	1.434	1.423	1.412	1.401	1.392	—
		82.00	—	1.541	1.540	1.533	1.516	1.503	—
4. „	<i>p</i> -Dibromobenzene	75.60	1.358	1.357	1.360	1.357	1.353	—	—
		90.80	—	1.404	1.420	1.416	1.410	—	—
5. „	<i>m</i> -Dinitrobenzene	35.12	—	1.432	1.418	1.411	1.401	1.378	—
		66.64	—	—	1.857	1.837	1.811	1.763	—
6. „	Benzoic acid	9.64	—	—	1.181	1.113	1.129	1.109	—
		14.48	—	—	1.206	1.211	1.202	1.191	—
7. Toluene	Naphthaline	66.00	—	—	1.498	1.495	1.498	1.477	1.473
		82.00	—	—	—	1.630	1.606	1.588	1.579
8. „	Acenaphthene	24.50	—	1.321	1.311	1.293	1.290	1.280	—
		40.00	—	—	1.509	1.480	1.476	1.456	—
9. „	<i>o</i> -Nitrophenol	182.50	—	—	2.436	2.366	2.310	2.260	2.213
		487.00	—	—	—	3.671	3.572	3.340	3.273
10. CCl ₄	Naphthaline	28.00	—	—	1.279	1.268	1.252	1.238	1.229
		45.60	—	—	—	—	1.400	1.386	1.370

THE VARIATION OF RELATIVE VISCOSITY WITH TEMPERATURE. ORGANIC SOLUTES IN NON-AQUEOUS SOLVENTS

BY A. C. CHATTERJI AND A. N. BOSE

A fairly comprehensive study of the temperature dependence of relative viscosity (η_s/η_0) of concentrated and supersaturated solutions of non-electrolytes in non-aqueous solvents has been made. The observed values of $\partial/\partial t_1 \left(\frac{\eta_s}{\eta_0} \right)$ can be divided into three categories, viz., (i) having approximately zero variation, (ii) having positive value, and (iii) having negative value for the variation of relative viscosity. In majority of cases the results can be explained by Rabinovich's solvate hypothesis and the depolymerisation hypothesis of Applebey

In a previous paper (Chatterji and Ram Gopal, *J. Indian Chem. Soc.*, 1947, **24**, 455) the variation of relative viscosity with temperature of aqueous solutions of electrolytes and a few non-electrolytes was studied. Several general conclusions about the variation of relative viscosity with temperature, based on the concept of depolymerisation of associated solvent molecules and on the hydrate hypothesis, were arrived at. It was suggested that these might be found useful in explaining further work on this subject.

In this paper attempt has been made to test the validity of the above conclusions. Moreover, this investigation is an extension of a previous work on the determination of viscosity of supersaturated aqueous solutions to supersaturated non-aqueous solutions, with a view to finding out the effect of viscosity on the release of supersaturation from such solutions.

The viscosity of non-aqueous solutions has not been very widely studied. However, important investigations in this direction were undertaken by Wagner and Mühlenbein (*Z. physikal. Chem.*, 1906, **46**, 867), Bramley (*J. Chem. Soc.*, 1916, **109**, 10, 434), Kendall and Monroe (*J. Amer. Chem. Soc.*, 1917, **39**, 1802), Dunstan and Thole ("Book on Viscosity of Liquids", 1914, p. 43), Taimni (*J. Phys. Chem.*, 1928, **32**, 604; 1929, **33**, 56), Briscoe and Reinhart (*ibid.*, 1942, **46**, 3, 387) and others. Most of the above workers studied the viscosity of the mixture and its variation with concentration.

Briscoe and Reinhart (*loc. cit.*), however, studied the effect of temperature on the relative viscosity of non-electrolytes and electrolytes in non-aqueous solvents and concluded that the relative viscosity decreased with temperature for all solutions studied except that of potassium iodide in glycerol. The concentration taken by them was not very high and, moreover, the solutions compared at different temperatures, though having nearly equal concentrations, were by no means exactly equal in concentration. For example in Table I of their paper (p. 389.), the temperature increased from 25° to 60° and the relative viscosity decreased from 1.0355 to 1.0305 but at the same time the

etc., no appreciable heating effect is observable in the case of cinnamic acid. Like cinnamic acid, other water-soluble unsaturated acids may be expected to behave in the same manner. Spontaneous crystallisation of fumaric and maleic acid solutions shows clearly (Table II) that $T_s - T$ appears to be almost independent of the degree of heating.

A more detailed examination of the effect of preheating on solutions of these acids is summarised in Table IV.

TABLE IV

(Hours of heating are given in brackets.)					
	Cinnamic acid		Fumaric acid		Maleic acid*
S_{w100}	T	S_{w100}	T	S_{w100}	T
0.20	50.8(2), 50.6(6), 50.4	2.5	44.2(2), 44.4(4), 44.2(10)	190.0	38.2(2)
0.40	63.6(6), 63.8(6), 63.4(12)	3.75	59.4(2), 59.2(4), 59.0(6), 54.6(10)	150.0	40.0(2)
0.60	68.6(6), 68.4(12), 68.6(16)	4.38	59.4(2), 60.0(4), 58.4(8)	175.0	45.2(2)
		5.00	64.8(2), 64.2(4), 64.0(6), 62.8(12)	220.0	59.6(2)

The heating in these experiments was performed after the experiments on crystallisation given in Table II were over. On comparing these cases with others e. g. benzoic acid, which inspite of its easy crystallisation from water has an appreciable heating effect, it appears that unsaturation of these acids has something to do with the small effect of heating on the values $T_s - T$. This is only a tentative suggestion in the absence of more data.

The author takes this opportunity to thank Dr. A. C. Chatterji under whose supervision some of the experimental part of the work was carried out and who has always shown a very keen interest in these investigations.

* After six hours of heating some solid, insoluble substance appeared at the bottom of the sealed tube. Due to this, crystallisation started even earlier than the attainment of these temperatures.

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TABLE III

Substance.	λ (numerical values)	$T_s - T$	$(T_s - T) \lambda$
KCNS	6100 cals.	13.0	79300
NaClO ₃	5600	12.0	67200
NH ₄ NO ₃	6320	10.3	65016
BaCl ₂	6700	25.6	171520
CS (NH ₂) ₂	(?)	11.2	—
CO (NH ₂) ₂	3641	13.1*	47697
(NH ₄) ₂ C ₂ O ₄	11500	12.6	144900
C ₆ H ₅ .CO ₂ H	7690†	17.7	136118
Ph.CH : CH.CO ₂ H	7491†	17.0 (?)	127347

* See *J. Indian Chem. Soc.*, 1943, 20, 183.

† Calculated from Williamson's equation (*Trans. Faraday. Soc.*, 1944, 40, 435) viz. :

$$\Delta H_{(Sol)} = RT_s^2 \left(\frac{dm}{dT} \right)_{Sat} \left[\left(\frac{d \ln f_2}{dm} \right)_{T_s} \left(\frac{1}{m} \right)_{Sat} \right]$$

valid for anhydrous non-electrolytes. As the solubility of these acids is very small, an approximation is made by putting the activity coefficient f_2 equal to unity. Hence the above equation simplifies to

$$\Delta H_{(Sol)} = RT_s^2 \left(\frac{dm}{dT} \right)_{Sat} \times \left(\frac{1}{m} \right)_{Sat}$$

The results given in Tables I, II and III show that $T_s - T$ for most of the solutes is, in general, fairly constant and almost independent of T_s , and further that the value of $(T_s - T) \lambda$ is round about 70,000 cal. for KCNS, NaClO₃ and NH₄NO₃.

It is a general phenomenon that prolonged and continuous heating helps to stabilise solutions against spontaneous crystallisation. A few notable exceptions to this general rule are the solutions of KI, KBr, KNO₃ and KClO₄ etc. as has been pointed out in earlier papers* and a probable explanation of this anomaly has been suggested in a recent communication (*J. Indian Chem. Soc.*, 1947, 24, 284) from this laboratory. The behaviour similar to that of KI, KBr and KNO₃ etc., has been noticed in the case of cinnamic, fumaric and maleic acids also. Whereas the effect of preheating is prominently displayed (Table I) by benzoic acid, ammonium oxalate and thiourea

*Even if stabilising effect does occur in these cases under very prolonged heating (cf. Jaffé, *Z. physikal. Chem.*, 1903, 43, 565,) it is only very slight and is negligible in comparison to that in other cases.

A somewhat incorrect statement occurs in an earlier paper of mine (*J. Indian Chem. Soc.*, 1943, 20, 187; second para. line 5). The line should read "Jaffé (*loc. cit.*) has shown $T_s - T$ can be increased even in KNO₃ by intensive *heating*" and not 'intensive filtration' as was published. However, this does not in any way invalidate my previous statements as the difference among the various categories is quite distinct and marked.

Ammonium oxalate**			Benzoic acid.		
T_s	T	$T_s - T$	T_s	T	$T_s - T$
40°	26.8,...	13.2	45°	28.0,25.0*	17.0
45°	32.4,30.2,26.0*	12.6	50°	32.2,30.0,26.0	17.8
50°	37.6,30.0*	12.4	55°	36.2,32.2,26.0	18.8
55°	42.0,39.0,35.6	13.0	60°	43.0,42.2,36.0	17.0
60°	47.0,37.0,27.6	19.0	65°	47.2,44.6,46.4	17.8
65°	52.8,50.0,46.2	12.2	70°	52.4,50.2,51.0,46.0,46.0	17.6
70°	58.0,56.6,51.0,50.0	12.0	75°	57.4,57.8,56.8,53.6,52.6	17.6
75°	62.2,62.0,60.0,55.4	12.8	80°	62.2,63.0,60.2,54.0	17.8
80°	67.8,67.2,66.4	12.2			
		Mean 12.6			Mean 17.7
Barium chloride.					
T_s	T	$T_s - T$	T_s	T	$T_s - T$
55°	30.0*				
60°	34.2,30.2,25.0*	25.8			
65°	40.0,38.6,25.0*	25.0			
70°	43.2,35.6,25.6*	20.8			
75°	49.2,45.0,32.4*	25.8			
80°	56.8,55.2,48.6	21.2			
		Mean 25.6			

** Solubility of ammonium oxalate has been determined in this Department by Mr. M. R. Nayar. The values at various temperatures are :—

Temp. ...	40°	50°	60°	70°	80°
$S_{w 100}$ (g.)	10.0	13.19	16.96	21.9	27.37

TABLE II

1. Cinnamic acid			2. Fumaric acid.		
$S_{w 100}$	T	$T_s - T$	$S_{w 100}$	T	
0.10	43.8,43.0,43.6,43.6		2.00	39.4,40.2,39.8	
0.20	52.0,51.2,52.0,51.8		2.50	45.0,44.8,44.8	
0.80	57.8,56.4,57.0,57.2		3.125	50.0,49.4,50.2	
0.40	67.4,69.0,67.0,66.8		3.75	56.6,56.8,55.4,56.8	
0.50	72.2,72.4,72.4,72.4	17.0	4.375	60.0,60.0,60.4	
at $T_s = 45°$	28.0,27.8,28.0		5.00	65.2,66.0,65.6	
			5.625	68.4	
3. Maleic acid.					
$S_{w 100}$	T				
100	25.0				
130	34.2,34.0,33.4				
150	42.2,42.8,42.0				
175	45.4,44.0,44.2				
200	51.8,52.2,52.2				
220	61.0,59.6,59.4				

As the solubilities of cinnamic, fumaric and maleic acids are not known, only the concentration of the solute in solution is given in Table II. In Table III are given the values of $T_s - T$, obtained from Table I and Table II (1), λ , the values of the heats of solution in cases where available, and the product $(T_s - T) \lambda$.

SUPERSATURATION LIMITS OF SOLUTIONS. PART V.

BY RAM GOPAL

The work on the limits of supersaturation in aqueous solutions has been further extended. The results obtained confirm the previous observations that in most cases $T_s - T$ for any particular solute is almost independent of T_s . Further, preheating has been found to have very little effect on $T_s - T$ in solutions of cinnamic, fumaric and maleic acid. Unsaturated nature of these acids is assumed to be responsible for this behaviour.

In continuation with the previous work on the limits of supersaturation (*J. Indian Chem. Soc.*, 1943, 20, 183; 1944, 21, 103, 145; 1947, 24, 279) more substances have been studied. The experimental method is the same as given in the first paper of this series. In Tables I and II are recorded the results obtained.

In all the tables T_s denotes the saturation temperature, T , the temperature of spontaneous crystallisation, and $T_s - T$, the difference between the saturation temperature T_s and first T . Temperature figures marked with an asterisk signify that crystallisation did not occur down to this temperature. $S_{w 100}$ denotes the amount of substance in g. in 100 g. of water.

TABLE I

Potassium thiocyanate.			Sodium chlorate.		
T_s .	T .	$T_s - T$.	T_s .	T .	$T_s - T$.
40°	32.0, 28.8, 26.5, 20.0	8.0 (?)	45°	23.1	
45°	31.2, 30.4, 19.4	13.8	50°	39.2, 34.6, 32.8	10.8
50°	58.8, 33.4, 18.3	13.2	55°	45.0, 35.0*, 30.0*	10.0
55°	42.0, 38.4, 36.2	13.0	60°	47.8, 47.2, 40.6	12.2
60°	46.0, 41.2, 37.8	14.0	65°	47.8, 26.8, 28.0*	17.4 (?)
65°	54.2, 52.2, 50.8, 48.2	10.8	70°	58.2, 44.4, 58.6, 45.2	11.8
			75°	61.2, 61.4, 65.2, 25.0	18.8
Mean 13.0			Mean 12.0		
Thiourea.			Ammonium nitrate.		
T_s .	T .	$T_s - T$.	T_s .	T .	$T_s - T$.
45°	33.0	12.0	40°	29.4, 29.0, 29.8	10.6
50°	37.8, 25.0*	11.2	45°	35.2, 33.0, 32.8	9.8
55°	43.8, 43.4, 38.0	11.2	50°	39.0, 39.2, 39.2, 38.8	11.0
60°	49.4, 49.2, 48.6, 43.8	10.6	55°	44.0, 44.8, 42.8, 42.0	11.0
65°	52.8, ...	12.2	60°	51.0, 50.8, 50.8, 51.4	9.4
70°	59.6, 59.8, 48.2	10.4	65°	53.2, 51.2, 52.8, 52.6	11.8
75°	64.3, 64.2, 58.2, 46.4	10.2	70°	62.0, 59.0, 57.6, 57.2	8.0
			75°	65.2, 61.0, 64.8, 65.0	9.8
Mean 11.2			Mean 10.3		

TABLE II

Total fat taken	5.934 g.
Wt. of tristearin obtained (I)	1.419
Wt. of mono-azelaol and di-azelaol glycerides (II)	1.39
Saponification of (II)	295.6
Wt. of mono-azelaol glycerides from S.V.	1.242
Wt. of mono-azelaol from equivalent	1.25

The weight of mono-azelaol glycerides could be checked by taking equivalent weight of the mixture (I), as the saturated acid in the glyceride is known to be stearic acid.

Hence, the composition of fat is as follows :—

	Found,	Taken.
Tri-saturated glyceride	23.84%	25.76%
Mono-unsaturated di-saturated glyceride	23.42	24.25

It will be seen from the above table that the composition of the fat, found by the above procedure, agrees within 5% of the theoretical as regards the tri-saturated glycerides (GS_3) and di-saturated mono-unsaturated glycerides (GS_2U).

As in our synthetic fat, stearic acid is the only saturated acid we could have calculated the mono-saturated di-unsaturated glyceride (GSU_2), but we have not done so as it would mean only an additional arithmetical computation.

We believe therefore that this method is suitable for estimating tri-saturated (GS_3) and di-saturated mono-unsaturated (GS_2U) glycerides only. The estimation of the quantity of mono-saturated di-unsaturated (GSU_2) will be uncertain and will not be accurate as the errors in estimating GS_3 and GS_2U will be multiplied in the estimation of GSU_2 .

MAHARAJA PARATAPSIJIH CHEMICAL LABORATORY,
SIR PARASHURAMBHAU COLLEGE, POONA 2.

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quantity of saturated acids present as GSU_2 can be calculated from the difference between the total saturated fatty acids and the saturated fatty acid present in GS_3 and GS_2U . This, however, involves the assumption that the saturated fatty acids are evenly distributed in the three types of glycerides. The method of Kartha and Menon appears to be straight forward and has the advantage that it requires small quantities of fats. The method has not been tested, however, so far for its accuracy on synthetic fats of known glyceride composition. We have prepared a synthetic fat from fully saturated glyceride (GS_3), di-saturated mono-unsaturated, (GS_2U), mono-saturated di-unsaturated (GSU_2) and tri-unsaturated (GU_3), and we have estimated the component glycerides using Kartha and Menon's method. The results are described below.

EXPERIMENTAL

Tristearin was prepared by using the method of Clarkson and Malkin (*J. Chem. Soc.*, 1934, 666).

Triolein.—Oleic acid (Merck) was converted into its methyl ester and fractionally distilled. The main fraction was hydrolysed and the oleic acid distilled. The acid did not show the presence of linolic or linolenic acids. This oleic acid was converted into triolein in the usual manner. The product obtained was water-white and had iodine value (Wijs), 86.5 (I. V. calc., 86.2).

Mono-stearo di-olein was prepared from pure oleic acid and mono-stearin according to the method described by Daubert, Spiegl and Longenecker (*J. Amer. Chem. Soc.*, 1943, 65, 2144). The product had I.V. (Wijs), 56.82 (calc., 57.2).

Mono-oleo di-stearin was prepared by the method described by Daubert, *et al.*, (*loc. cit.*). The final product had I.V., 26.18 (calc., 28.4).

Table I gives the properties and composition of the fat prepared by mixing the above mentioned glycerides.

TABLE I

Composition of the fat.				Properties of the fat.			
					Obs	Calc.	
Tristearin	25.75%	Iodine value	...	42.75	42.6
Triolein	24.60	Sapon. value	...	188.1	189.6
1-Mono-stearo- 2 : 3-diolein			25.37	Titre test	...	41°	
1-Mono-oleo- 2 : 3-distearin			24.25	Acid value	...	Negligible	

The fat was oxidised by potassium permanganate following strictly the method adopted by Kartha and Menon (*loc. cit.*). The following table gives the relevant data for the calculations of the component glycerides.

INVESTIGATION OF SOME METHODS OF DETERMINING THE GLYCERIDE COMPOSITION OF FATS. PART I.

BY V. V. MHASKAR, N. L. PHALNIKAR* AND B. V. BHIDE

A synthetic fat from fully saturated, di-saturated mono-unsaturated, mono-saturated di-unsaturated glycerides has been prepared and the component glycerides have been estimated.

The work of Hilditch and several others have shown the importance of determining the glyceride composition of fats, as the physical properties of fats are modified considerably by the composition of the component glycerides (cf. Hilditch, "Chemical Constitution of Natural Fats", Oxford University Press, 1939, p. 181).

The method of estimating tri-saturated glycerides has been standardised, but some of the other methods require direct confirmation by analysis of mixtures of glycerides of known composition. Several saturated and unsaturated glycerides of known structure have been synthesised by the present authors and the applicability of the various methods of determining the glyceride composition, so far used, is being investigated.

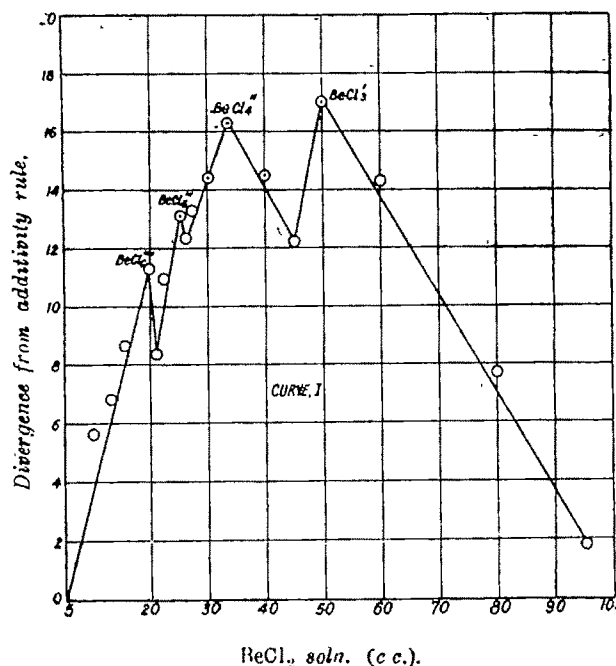
Kartha and Menon (*Proc. Ind. Acad. Sci.*, 1943, 17A, 114) claim to have developed a tentative method of determining the composition of fats containing di-saturated, mono-unsaturated glycerides (GS_2U) and di-unsaturated mono-saturated glycerides (GSU_2).

In a fat containing tri-saturated glycerides (GS_3), di-saturated mono-unsaturated (GS_2U), di-unsaturated mono-saturated (GSU_2) and tri-unsaturated glycerides (GU_3), oxidation will give a mixture of GS_3 and mono-azelaol di-saturated (GS_2A), diazelaol mono-saturated (GSA_2) and tri-azelaol glycerides (GA_3). Of these, the first (GS_3) is neutral and can be separated from the acidic products. This forms the basis of the method developed by Hilditch and Lea (*J. Chem. Soc.*, 1927, 3106) for estimating fully saturated glycerides in a fat. It has been found by Hilditch (*loc. cit.*, p. 406) that from a mixture of mono-azelaol di-saturated (GS_2A), di-azelaol mono-saturated (GSA_2) glycerides potassium bicarbonate extracts only the mono-azelaol di-saturated glycerides completely, and partly the di-azelaol mono-saturated glycerides. On the basis of this observation Kartha and Menon (*loc. cit.*) suggest that potassium bicarbonate extracts would give mainly mono-azelaol di-saturated glycerides containing a little of di-azelaol mono-saturated glycerides and from the saponification value of the mixture it is possible to calculate the quantity of GS_2U , and hence the composition of the fat as regards the GS_2U and GS_3 can be calculated with accuracy. For the calculation of GSU_2 Kartha and Menon suggest that in the mixture of fats, considered above, if GS_3 and GS_2U are known and the saturated acid content, if be known, the

* Junior Research Fellow, National Institute of Sciences of India.

DISCUSSION

The curve I (Fig. I) showing the divergence from the additivity rule in the conductometric measurements of BeCl_2 with NH_4Cl has four maxima, clearly demarkated by the corresponding minima. The compositions of the solutions at these maxima indicate the formations of $[\text{BeCl}_3]'$, $[\text{BeCl}_4]''$, $[\text{BeCl}_5]'''$ and $[\text{BeCl}_6]^{iv}$ in solution. These observations clearly indicate that there are four



chloroberyllates, analogous in composition to the four fluoberyllates, already reported. A comparative study of the fall in conductivity due to complex formations reveals that chloroberyllato complexes are much more unstable than the corresponding fluoberyllates. The fact that chloro complexes are very unstable and that these are four in number make it difficult to select out physico-chemical methods for their study. However, attempts are being made to substantiate the conclusion derived from the conductivity measurements by other physico-chemical measurements.

In conclusion the author expresses his deep sense of gratitude to Prof. P. B. Sarkar, Dr. es. Sc., F. N. I., for his encouragements, helpful suggestions and laboratory facilities. The author is indebted to Krishnarpan Charity Trust for the award of an endowment.

0.1%. The mean of the three values of resistance was always taken. The thermostat was so adjusted that the temperature varied within 0.05° . The platinum electrode was deplatinised and recoated with a thin deposit of spongy platinum. In consideration of the precautions that have been taken in every step, it is clear that the probable error due to all sources cannot exceed 0.2%.

The reciprocal of the observed resistance *i.e.*, conductance was sufficient to draw the curve. So the cell constant was not determined. The conductances of the constituents, namely beryllium chloride and ammonium chloride solutions, were measured in the way as tabulated below (Table I), and the divergence from the additivity rule has been plotted against composition.

TABLE I
Conductance measurements with BeCl₂ and NH₄Cl

Temp. = 32.2° .

1		2	3		4	5	6		7	8
$M/20\text{-BeCl}_2 \text{ soln. (c.c.).}$		Conductance of (1) $\times 10^3 = C_1$.	$M/20\text{-NH}_4\text{Cl soln. (c.c.).}$		Conductance of (3) $\times 10^3 = C_2$.	$C_1 + C_2 = C_3$.	$M/20\text{-BeCl}_2 \text{ soln. (c.c.).}$		Conductance of (6) $\times 10^3 = C_4$.	$(C_3 - C_4) \times 10$.
Water added (c.c.).			Water added (c.c.).				$M/20\text{-NH}_4\text{Cl soln (c.c.).}$			
5	95	2.726	95	5	27.35	30.076	5	95	29.94	1.360
10	90	5.137	90	10	26.39	31.527	10	90	30.82	7.070
13	87	6.579	87	13	25.37	31.949	13	87	31.17	7.790
15	85	7.449	85	15	24.90	32.349	15	85	31.33	10.19
20	80	9.803	80	20	26.61	33.473	20	80	32.21	12.63
21	79	10.27	79	21	23.21	33.48	21	79	32.51	9.70
22	78	10.80	78	22	23.05	33.85	22	78	32.62	12.30
25	75	12.21	75	25	22.19	34.40	25	75	32.96	11.40
26	74	12.52	74	26	21.85	34.37	26	74	33.01	13.60
27	73	13.14	73	27	21.54	34.68	27	73	33.22	14.60
30	70	14.45	70	30	20.81	35.26	30	70	33.68	15.80
33.35	66.65	15.67	66.65	33.35	19.78	35.45	33.35	66.65	33.68	17.70
40	60	18.75	60	40	17.89	36.64	40	60	35.05	15.90
45	55	20.83	55	45	16.51	37.34	45	55	35.99	13.50
50	50	23.10	50	50	15.18	38.23	50	50	36.39	18.40
60	40	27.13	40	60	12.20	39.33	60	40	37.75	15.80
80	20	34.95	20	80	6.256	41.206	80	20	40.30	9.060
95	5	40.93	5	95	1.020	42.55	95	5	42.24	3.100

Difference from the least divergence from the additivity rule in each case has been plotted against composition (Fig. 1, curve I).

CHLOROBERYLLATES

By BHUPESH CHANDRA PURKAYASTHA

From conductometric measurements it has been shown that four chloroberyllate ions, namely, $[\text{BeCl}_3]'$, $[\text{BeCl}_4]''$, $[\text{BeCl}_5]'''$ and $[\text{BeCl}_6]^{iv}$ exist in solution.

In a previous communication (Purkayastha, *J. Indian Chem. Soc.*, 1947, 24, 257) it has been shown that four fluoberyllate ions, namely, $[\text{BeF}_3]$, etc., $[\text{BeF}_3]'$, $[\text{BeF}_4]''$, $[\text{BeF}_5]'''$ and $[\text{BeF}_6]^{iv}$ exist in solution and from the facts stated therein, it has been argued that beryllium, analogous to its neighbours, aluminium and magnesium in the periodic table, may form hexa-co-ordinated ions as far as our observations with fluoro compounds are concerned. Several double salts of aluminium and magnesium chlorides with alkali chlorides are described, but not a single double salt of BeCl_2 with alkali chloride is known. The failure in the isolation of double salts with beryllium chloride does not, however, exclude the probability of the existence of chloroberyllate ions in solution. A search demonstrating the existence and composition of the chloroberyllate ions in solution from conductometric measurements forms the subject matter of the present investigation.

EXPERIMENTAL

Beryllium Chloride.—A solution of BeCl_2 was prepared by treating a saturated solution of beryllium sulphate with calculated amount of barium chloride. The barium sulphate was filtered off through a silica bed. The concentration of the solution was ascertained by estimating both beryllium and chlorine. Be was precipitated as hydroxide with ammonia and ignited to BeO . Chlorine was estimated volumetrically by Volhard's method. The ratio of Be to Cl was found to be 1 : 1.982.

Ammonium Chloride.—The stock solution was prepared with Merck's NH_4Cl of reagent quality. Ammonia was estimated by distillation with alkali and by absorbing the distillate in a standard acid and titrating back the excess acid. Chlorine was estimated volumetrically in the same way as was done in the previous case.

Beryllium sulphate ($\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$) was prepared by digesting Kahlbaum's beryllium carbonate in H_2SO_4 and crystallising the product. The crystals were dissolved in warm water. The solution was acidified with sulphuric acid and recrystallised. The crystals were washed three times with ice-cold water and finally with alcohol till free from acid.

The conductivity apparatus was fitted with thermoionic valve amplifiers and so the experimental error in determining resistance was brought within

acid was purified by distillation in *vacuo* as a colourless, viscous liquid, b. p. 170°-173°/3 mm., yield 60%. (Found : C, 76.68 ; H, 8.75. $C_{13}H_{18}O_3$ requires C, 75.72 ; H, 8.73 per cent).

4 : 5 : 7-Trimethyltetralone-1 (XXI).—The above acid was cyclised by using the method employed for the ring-closure of γ -(*p*-cymyl-2)- α -methylbutyric acid (Sukh Dev and Guha, *loc. cit.*). In this case it became necessary to reflux the reaction mixture for 15 minutes in order to dissolve all the aluminium chloride. The product was obtained as a colourless liquid, b. p. 155-59°/9 mm., yield 77%. (Found : C, 83.00 ; H, 8.72. $C_{13}H_{16}O$ requires C, 82.97 ; H, 8.51 per cent).

The 2 : 4-dinitrophenylhydrazone was prepared by the sulphuric acid method and recrystallised from benzene (containing a small amount of petrol, b. p. 86-90°) in deep red plates, m. p. 231-32°.

1 : 6 : 8-Trimethyl-4-isopropyl-naphthalene (XXIII).—*iso*Propyl magnesium bromide was reacted with the above ketone (10.0 g) in the same way as described under 1 : 3 : 6-trimethyl-4-isopropyl-naphthalene.

The crude carbinol (11.0 g.), which was obtained as a reddish viscous syrup, was dehydrated with 90% formic acid (20 c.c.) in the usual manner. The crude unsaturated hydrocarbon was purified by distillation in vacuum as a colourless, mobile liquid, b. p. 130°-35°/3 mm., yield 6.0 g. (53% overall yield) ; quite a good amount of the substance was retained as a resinous residue in the distillation flask.

The hydrocarbon (6.0 g.) was dehydrogenated with sulphur (1.0 g.) first at 230° for $\frac{1}{2}$ hour and finally at 260° for another $\frac{1}{2}$ hour. The methylcadalene was worked up in the usual manner and purified by distillation over sodium in vacuum as a colourless, mobile liquid, b. p. 144-47°/3 mm., yield 3.6 g. (Found : C, 90.34 ; H, 9.81. $C_{16}H_{20}$ requires C, 90.56 ; H, 9.43 per cent).

The *picrate* was repeatedly crystallised from alcohol till the m. p. became constant ; dark red needles, m. p. 108°-108.5°.

The *trinitrobenzene compound* was twice recrystallised from 80% acetic acid in orange needles, m. p. 118°-18.5°.

The author's thanks are due to Prof. P. C. Guha, for the kind interest he has taken in this work.

isopropyl bromide (15.6 g., 1.6 mol.) and ether (75 c.c.). The Grignard solution was chilled in an ice-salt bath and the above ketone (15.0 g., 1 mol.) in dry ether (75 c.c.) was added in a thin stream with swirling (10 mins.). The reaction mixture became brownish with the separation of a viscous heavy liquid. The mixture was kept as such for 15 minutes and it was then allowed to reach the room temperature (25°) during $\frac{1}{2}$ hour. The reaction was completed by refluxing for $3\frac{1}{2}$ hours and then leaving overnight (13 hours). The product was decomposed with ice and ammonium chloride and worked up in the usual manner. The crude carbinol was dehydrated by heating with 20 c.c. of acetic anhydride for 3 hours on a steam-bath and the reaction mixture was fractionated from a modified Claisen's flask. The required unsaturated hydrocarbon distilled as a colourless, mobile liquid, b.p. 135-40°/3.5 mm., yield 13.0 g. (76%).

The dihydromethylcadalene (13 g.) was dehydrogenated with selenium (7 g.) (see under 5-methylcadalene) to give 3-methylcadalene, which was purified by repeated distillations over sodium, as a colourless, mobile liquid, b.p. 145°/4 mm., yield 60%. (Found: C, 91.17; H, 9.40. $C_{16}H_{20}$ requires C, 90.56; H, 9.43 per cent).

The *picrate*, prepared in the usual manner, was recrystallised thrice from alcohol as silky, orange needles, m.p. 162-63°. The *trinitrobenzene compound* was prepared by the method described under 5-methylcadalene and recrystallised from 80% acetic acid in silken yellow needles, m.p. 165°.

1 : 6 : 8-Trimethyl-4-isopropyl-naphthalene (XXIII)

β-(2-m-Xyloyl)-propionic Acid (XVII) — Succinic anhydride (35.0 g., 1 mol.) was condensed with *m*-xylene (40.8 g., 1.1 mol.) in a dry nitrobenzene (150 c.c.) solution in presence of anhydrous aluminium chloride (104 g., 2.2 mols.). [For details, see under *β*-(*p*-toluyl)-*α*-methylpropionic acid]. Yield of the crude product (m.p. 107°-9°) was quantitative. The product was recrystallised from 5 parts of a mixture of benzene (3 parts) and ligroin (b.p. 80-90°, 4 parts) in colourless, long, fine needles, crystallising in stars, m.p. 111-12°, yield 62-65 g. (86-90%) (Barnet and Sanders, *loc. cit.*, m.p. 108°, 111°-12°, 114°).

Methyl β-(2-m-Xyloyl)-propionate (XVIII).—The above acid (60.0 g.), methanol (120 c.c.) and concentrated sulphuric acid (8.0 c.c.) were refluxed for 7 hours and the product worked up in the usual manner. The ester was purified by distillation, b.p. 151-52°/2.5 mm., yield, 56.0 g. (87.5%).

γ-(2-m-Xylyl)-*γ*-methylvinylacetic Acid (XIX).—The reaction was carried out in exactly the same way as given under *γ*-(*p*-tolyl)-*γ*:*α*-dimethylvinylacetic acid, yield 70-80%.

γ-(2-m-Xylyl)-valeric Acid (XX).—The crude acid (12.0 g.), hydriodic acid (*d* 1.7, 60.0 g.) and red phosphorus (8.0 g.) were refluxed at 130-140° for 30 hours. The duct was worked up in the usual manner. The reduced

Solvent.	Solute.	*Conc.	20°	25°	30°	35°	40°	45°	50°
11.	<i>o</i> -Nitroaniline	1.996	—	—	1.056	1.052	1.050	1.046	1.041
		8.000	—	—	—	1.265	1.256	1.250	1.223
12.	CHCl ₃ Acenaphthene	24.200	—	1.637	1.596	1.560	1.518	—	—
		34.000	—	1.780	1.747	1.703	1.680	—	—
13.	<i>m</i> -Dinitrobenzene	33.320	2.068	2.022	1.975	1.920	1.874	—	—
		40.860	—	2.243	2.202	2.142	2.088	—	—
14.	Acetone Naphthalene	44.83	1.569	1.544	1.535	1.524	1.514	—	—
		68.00	—	1.780	1.752	1.731	1.721	—	—
15.	<i>o</i> -Nitroaniline	117.00	3.999	3.870	3.780	3.651	3.568	—	—
		280.00	—	7.455	7.200	6.873	6.630	—	—
16.	MeOH Acenaphthene	2.25	—	1.030	1.010	1.008	1.007	1.006	—
		3.50	—	—	1.030	1.029	1.031	1.028	—
17.	Acetanilide	41.50	1.823	1.795	1.764	1.736	1.710	—	—
		64.00	—	—	2.226	2.178	2.117	—	—
18.	Benzoic acid	68.00	—	2.362	2.300	2.253	2.222	2.204	—
		88.00	—	—	2.613	2.563	2.512	2.448	—
19.	Diphenylamine	20.00	—	1.467	1.420	1.399	1.383	1.363	—
		39.40	—	1.827	1.780	1.743	1.725	1.663	—
20.	Urea	20.00	—	1.754	1.713	1.685	1.653	1.613	—
		30.00	—	2.240	2.135	2.090	2.040	1.997	—
21.	Propyl Benzoic acid alcohol	40.00	—	1.426	1.423	1.420	1.415	1.405	—
		56.00	—	—	1.699	1.586	1.570	1.559	—
22.	Urea	2.56	—	1.074	1.065	1.074	1.070	1.064	—
		4.00	—	1.124	1.126	1.123	1.116	1.110	—
23.	<i>iso</i> Pro- Dibromopyl benzene alcohol	11.52	—	0.9486	0.9586	0.9760	0.9810	0.9816	—
		18.00	—	—	0.9472	0.9672	0.9699	0.9844	—
24.	<i>n</i> -Butyl Naphthalene alcohol	14.95	—	—	0.920	0.9204	0.9270	0.9250	0.929
		23.00	—	—	—	0.9882	0.9990	0.9960	0.9968
25.	Acetic Naphthalene acid	15.51	—	—	1.142	1.133	1.116	1.105	1.100
		56.00	—	—	—	—	1.159	1.137	1.128

* Concentration is expressed in grams of solute in 100 g. of solvent.

DISCUSSION

From the results recorded above the solutions can be divided into three categories (cf. Chatterji and Bose, *J. Indian Chem. Soc.*, 1948, 25, 39).

TABLE II

Solutions giving approximately zero $\frac{\delta}{\delta t} \left(\frac{\eta_s}{\eta_0} \right)$.

Solvent	Solute.
1. Hexane	Naphthalene
2. Benzene	<i>p</i> -Dibromobenzene
3. Methyl alcohol	Acenaphthene

TABLE III

Solutions giving positive variations of $\frac{\delta}{\delta t} \left(\frac{\eta_s}{\eta_0} \right)$.

Solvent	Solute.
1. <i>n</i> -Butyl alcohol	Naphthalene
2. <i>iso</i> Propyl alcohol	<i>p</i> -Dibromobenzene

TABLE IV
Solutions giving negative variations of $\delta/\delta_t \left(\frac{\eta_s}{\eta_o} \right)$.

Solvent.	Solute.	Solvent.	Solute.
1. Hexane	Diphenylamine	11. Toluene	<i>o</i> -Nitrophenol
2. CCl ₄	Naphthalene	12. CHCl ₃	<i>m</i> -Dinitrobenzene
3. „	<i>o</i> -Nitroaniline	13. „	Acenaphthene
4. Benzene	Naphthalene	14. MeOH	Benzoic acid
5. „	<i>m</i> -Dinitrobenzene	15. „	Urea
6. „	Benzoic acid	16. „	Acetanilide
7. Toluene	Naphthalene	17. „	Diphenylamine
8. „	Acenaphthene	18. Acetic acid	Naphthalene
9. Acetone	Naphthalene	19. <i>n</i> -Propyl alcohol	Benzoic acid.
10. <i>n</i> -Propyl alcohol	Benzoic acid		

Solutions of the First Category (i).—It was suggested in the previous paper that if the solvent consisted of simple molecules and the solute did not interact with the solvent in any way, the value of $\frac{\delta}{\delta_t} \left(\frac{\eta_s}{\eta_o} \right)$ should be approximately zero. When we apply this to the solution in category (i) given above, we find, that the two solutions, viz., hexane—naphthalene and benzene—*p*-dibromobenzene confirm the above conditions. But methyl alcohol—acenaphthene gives approximately zero temperature coefficient even though methyl alcohol is associated in the pure state, and therefore it appears to be an apparent anomaly.

Solutions of the Second Category (ii).—The solutions in the second category given above consists of the solvents (*n*-butyl and isopropyl alcohols) which are associated and the solutes (naphthalene and *p*-dibromobenzene) do not appear to affect the solvent to any appreciable extent as they are non-polar. Therefore, according to the generalisation drawn in the previous paper (*loc. cit.*) they should give a positive value for $\frac{\delta}{\delta_t} \left(\frac{\eta_s}{\eta_o} \right)$ and this is exactly what we find here.

Solutions of the Third Category (iii).—In group (iii) of the previous paper solutions consisting of simple solvent molecules and solutes forming easily breakable solvates with solvents were predicted to give negative value for $\frac{\delta}{\delta_t} \left(\frac{\eta_s}{\eta_o} \right)$. Whereas group (iv) consisting of associated solvents and solutes forming solvates, should give either a positive or a negative value for $\frac{\delta}{\delta_t} \left(\frac{\eta_s}{\eta_o} \right)$, depending upon which of the two factors, depolymerisation of solvents molecules or breaking up of solvate complexes, predominates.

As in this paper highly supersaturated solutions have been taken, the depolymerisation of the solvent must have been complete, and therefore the solvate effect predominates. The value of $\frac{\delta}{\delta_t} \left(\frac{\eta_s}{\eta_o} \right)$ at such a high concentration should be negative even in the case of group (iv) of the previous paper (*loc. cit.*).

For this reason instead of dividing the above solutions with negative temperature coefficient into two categories, we have put them into one. If we examine the group that gives negative value of $\frac{\delta}{\delta t} \left(\frac{\eta_s}{\eta_o} \right)$, we find that the system, mostly consisting of non-associated solvents and any solute, generally gives a lower negative value for $\frac{\delta}{\delta t} \left(\frac{\eta_s}{\eta_o} \right)$ than those in which the solvent is an associated liquid and the solute, generally a polar compound. But, there are, a few exceptions, such as toluene-*o*-nitrophenol, chloroform-acenaphthene, chloroform-dinitrobenzene, which give larger values of $\frac{\delta}{\delta t} \left(\frac{\eta_s}{\eta_o} \right)$ instead of low values.

On the other hand, propyl alcohol-benzoic acid and acetic acid-naphthalene give lower values of $\frac{\delta}{\delta t} \left(\frac{\eta_s}{\eta_o} \right)$ instead of higher ones.

Among these it has now been definitely proved that acetic acid molecules do not break up even in the gaseous state if the temperature is not very high, and hence depolymerisation effect should not play an important part; consequently the temperature variation should be small.

At this stage no definite explanation can be given for the other anomalies unless evidences are brought forward for the depolymerisation effects of solutes and their power to form association or complexes with the solvent molecules by quite independent methods.

Further work is in progress to bring forward such evidences by studying association and depolymerisation in binary mixtures by measuring the depression of their freezing points.

CHEMICAL LABORATORIES,
LUCKNOW UNIVERSITY,
LUCKNOW.

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CONDENSATION OF ALDEHYDES WITH MALONIC ACID. PART XXI.
CONDENSATION OF 5-BROMOVANILLIN. THE INFLUENCE OF
A BROMO GROUP IN ASSOCIATION WITH A HYDROXY
AND A METHOXY GROUP

BY PREM MOHANLAL MIRCHANDANI AND KANTILAL C. PANDYA

5 Bromovanillin is condensed with malonic acid and gives, instead of the expected cinnamic acid derivative, 5-bromo-3-methoxy-4-hydroxybenzylidene-malonic acid. Under special conditions the yield approaches 70%.

Earlier studies have shown that in the aldehyde-malonic acid condensations, in the presence of a trace of pyridine, the hydroxy group in the *ortho* and the *para* positions has on the whole a retarding influence (Kurien, Pandya, and Surange, *J. Indian Chem. Soc.*, 1934, 11, 823; Pandya and Vahidy, *Proc. Ind. Acad. Sci.*, 1936 4A, 140). With a methoxy group, on the other hand, the aldehyde condensed well and gave better yields (Pandya and Vahidy, *ibid.*, 1936, 4A, 134; 1937, 5A, 437). In the case of vanillin, which is 3-methoxy-4-hydroxybenzaldehyde, the yields were better than those obtained with protocatechuic aldehyde (3 : 4-dihydroxybenzaldehyde) (Pandya and Sodhi, *ibid.*, 1939, 9A, 511). It has also been found that a bromine group assists the reaction and increases the yield (Pandya and Miss Pandya, *ibid.*, 1943, 18A, 164; Gauri Shankar Gupta, Thesis, 1943, unpublished).

Vanillin-malonic acid condensations gave yields in 3½ hours of 51-61%; 5-bromovanillin gave yields rising up to 70% in 8 hours. Under ordinary conditions with 6 hours' heating and a trace of pyridine the yield was smaller, only 38%. The aldehyde melts at 163° and malonic acid decomposes long before that temperature is reached. To obviate this difficulty experiments with increasing amounts of pyridine were made, but the yields did not improve much. It is interesting to note that Perkin's method altogether failed to give any product, while Vorsatz' method of employing more pyridine (6 mols.) and keeping three weeks at room temperature succeeded. Robinson and Shinoda's method (*J. Chem. Soc.*, 1925, 1977) gave a fairly good yield (44%). In absolute alcoholic solution and with pyridine, the yield was 70%.

Another important point is that the product of the reaction is *not* the expected monobasic acid derivative, but is the dibasic malonic acid derivative, showing that here, under the conditions tried, bromine did not allow decarboxylation to occur. This has been found to be usual with heavy-weighted aldehydes (cf. Parts XVIII and XX, *this Journal*, 1947, 24, 437, 447.)

EXPERIMENTAL

5-Bromovanillin was prepared according to the method of Dakin (*J. Amer. Chem. Soc.*, 1920, 42, 493). Recrystallised from hot alcohol it melted at 153° (Dakin, m.p. 163-64°), yield 87%.

Condensation in the presence of a Trace of Pyridine.—5-Bromovanillin (1.15 g.), malonic acid (0.5 g.) and pyridine (0.07-0.08 c.c.) (1 : 1 : 0.2 mol.) were heated on a water-bath (98°) for 6 hours. No other change excepting the appearance of a slight yellow colour was noticed. After cooling, the mixture was extracted with ammonium carbonate solution (10%). The original aldehyde is soluble in sodium carbonate solution. About half the product went in solution. After filtration and acidification, a white precipitate was obtained melting at 220°; after several crystallisations from hot alcohol, the melting point became constant at 245° (decomp.). The yield of 5-bromo-3-methoxy-4-hydroxybenzylidene-malonic acid was 38% of theory. (The residue after treatment with alkali was the unreacted aldehyde).

In all the succeeding experiments, the identical product was obtained, as was shown by the mixed melting point and by other properties.

Condensation in the presence of Pyridine (1 mol.).—Aldehyde (1.15 g.), malonic acid (0.5 g.), 0.4 c.c. of pyridine (1 : 1 : 1 mol.) were heated together in the same way (6 hours). Foam and bubbles were observed. On repeating the above treatment, the identical acid in the same yield was obtained.

Condensation without any condensing agent.—(i). No reaction was found to take place after 6 hours' heating on a water-bath.

(ii). In a second experiment the reaction mixture was heated at 115-120° for 8 hours. The mixture had become of a light violet colour. The same acid in a lower yield (31%) was obtained; a great deal of the unused aldehyde was recovered.

Condensation in the presence of Pyridine (3 mols.).—The substances were taken in 1 : 1 : 3 mols. (1.15 g., 0.5 g. and 1.2 c.c.) and were heated on a water-bath for 6 hours. Evolution of a gas was noticed. The same acid in 31% yield was obtained.

Condensation by Perkin's Method.—The aldehyde (1.15 g.), freshly fused sodium acetate (0.5 g.) and acetic anhydride (0.8 c.c.) (1 : 1 : 2 mols.) were heated at 170-180° for 10 hours. The aldehyde was recovered unchanged.

Condensation at room temperature in the presence of Pyridine (7 mols.).—The same amounts of the aldehyde and malonic acid, with 2.8 c.c. of pyridine, were kept for 3 weeks at room temperature (25-35°). A yellow precipitate separating was taken out and therefrom the identical acid was recovered in the usual way but in a smaller yield (19%).

Condensation on a water-bath in the presence of pyridine (5 mols.) gave a 32% yield.

Condensation by Robinson-Shinoda's method (loc. cit).—Aldehyde (1.15 g.), malonic acid (1.6 g.), pyridine (2.1 c.c.) and piperidine (two drops) were heated on a water-bath (reflux condenser) for 3 hours. The flask was heated on the direct flame (wire gauze) for 15 minutes. A yellowish precipitate came down which after several crystallisations gave the same acid, m. p. 245° , yield 44% of theory.

When the aldehyde and malonic acid were taken with pyridine (1 : 1 : 2) and enough of absolute alcohol, and refluxed for over 8 hours on a water-bath, the yield was over 70%.

The acid obtained was insoluble in cold or hot water, ether, chloroform and benzene; sparingly soluble in cold alcohol, and quite soluble in hot alcohol, acetone and acetic acid.

It decolorised both bromine water and alkaline permanganate, suggesting unsaturation or a reducing (phenolic) group, or both. In alcoholic solution it gave a green colour with ferric chloride, indicating a phenolic group.

Equivalent weight, by titration with sodium hydroxide solution, was 155.4 and 155.6. The unsaturated monobasic acid, 3-methoxy-4-hydroxy-5-bromobenzylidene-acetic acid ($C_{10}H_9O_4Br$) requires 272.9, while the unsaturated dibasic acid, 3-methoxy-4-hydroxy-5-bromobenzylidene-malonic acid ($C_{11}H_9O_6Br$) requires 158.5.

The silver salt method and Rast's method of finding the molecular weight were both inapplicable as the acid decomposed under the conditions of the experiments.

Bromine was estimated by the fusion method with sodium peroxide. [Found: Br, 25.42, 25.66. The mono acid (above) $C_{10}H_9O_4Br$ requires Br, 29.30%, while the dibasic acid (above) $C_{11}H_9O_6Br$ requires Br, 25.24%].

Several of the usual methods for decarboxylating the dibasic malonic acid to the corresponding monobasic acid were tried, but without success. (Compare the corresponding acids from the two nitrosalicylaldehydes: Pandya, Saxena and Tinku, *J. Indian Chem. Soc.*, 1947, 24, 433, 443).

CHEMISTRY LABORATORY,
ST. JOHN'S COLLEGE, AGRA.

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REVIEW

Inorganic Chemistry—By Fritz Ephraim. Translated by P. C. L. Thorne and E. R. Roberts. Published by Gurney and Jackson, London; 1943; pp. 921; price 28sh.

The present volume is the fourth English edition of the well-known German Text, *Anorganische Chemie*, by Fritz Emphraim. Many new materials have been incorporated in the present edition in order to include the latest informations on some topics, relating particularly to valency, radioactivity, isotopes, and a few new compounds and reactions. On the whole, the book undoubtedly represents a marked improvement on its last edition, and will certainly maintain the high reputation which Ephraim's text-book has enjoyed since its first publication nearly a quarter of a century ago. It cannot be too strongly recommended to the teachers and advanced students of Inorganic Chemistry. Few text-books in science have survived such a long period of time without losing its popularity and usefulness, and that even after the death of its author. This, in itself, is an indisputable evidence of its merit. The present edition is very well got up, and the printing and binding leave nothing to be desired. There are, however, a few errors, typographical and factual, that have come to the notice of the reviewer. These are enumerated below so that they might be removed in the next edition of the book.

1. In the preface itself there is a mention of some figures on pp. 123, 755, 842, and 305. In the actual text, however, these pages are absolutely free from all figures.

2. On p. 3, it is written that "the product of the error and the momentum is equal to a constant, Planck's universal constant h ". This is obviously wrong and should be replaced by "the product of the errors in measuring the position and the momentum is equal to a constant etc...".

3. On p. 4, line 1, "to calculate the series of lines etc" should be replaced by "to calculate the frequencies of the series etc.."

On the same page in para 2, it is written that "the orbit nearest the nucleus is described as the K-level etc...". No distinction is made between the orbits and levels. This is rather confusing and inaccurate.

Again on the same page, towards the bottom, the spin quantum number, m_s , is defined as the direction of the electron spin in a magnetic field. There is no justification in ascribing the spin of the electron to an external magnetic field.

4. On p. 50, line 13 from the top, it is stated that "the variations of valency are, however, more often due to the fact that some of the compounds are electrovalency compounds and some covalency compounds etc...".

The statement is not a precise one.

5. On p. 55, last line, the bond angle 200° for F_2O should be 100° :

6. On p. 69, line 14 from the top, it is written that "in equal times equal numbers of atoms of the same radio-element are decomposed, which is characteristic of reactions of the first order." This is obviously wrong.

A confusion is made between number and concentration.

7. On p. 70, para 2, it is written that "the term mean life period indicates the number of atoms out of which one is disintegrated per day." This is not a correct and happy statement.

8. On p. 114, line 8 from the top, the word 'atomicity' has been used to mean molecular composition. This is rather unusual.

9. On p. 142, line 8 from the top :—"The low value for the hardness of graphite depends on the fact that in the ordinary test only the fourth and the weakest valency of the carbon atom comes into play, that is parallel to the cleavage plane. At right angles to these planes the hardness approaches that of the diamond".

The fact is, however, quite the contrary.

10. On p. 213, near the bottom, it is stated that Au, Pt and Pd are dissolved from the alloy in nitric acid etc. Obviously, nitric acid should be replaced by aqua regia.

11. On p. 231, line 2, the relative *masses* should be replaced by relative *numbers*; and in line 8, *polarisability* should be replaced by *polarising power*.

12. On p. 235, line 13, cuprous iodide is described as *pale yellow*; but we know it to be *white*.

13. On p. 287, Sugden's formulation of co-ordination compounds with semipolar singlet linkage might have been profitably omitted, as there is no theoretical and experimental justification behind it.

14. On p. 295, in the line below the table, it is stated that "the presence of H^+ ions retards the conversion of the violet into the green form". This has been wrongly translated and should be "..... retards the formation of the violet from the green form".

15. On p. 310, just over the heading *Cobaltammines and Chromammines* it is stated that "the cyanogen in these compounds can also be replaced by other radicals, but these substances have *not been studied* in detail. The translators have here overlooked the description and study of a large number of substituted cyano-cobaltates containing S_2O_3 , SO_3 and H_2O groups. These might have been included as interesting and welcome materials in the present edition.

16. On p. 383, line 1, the words "radii of univalent cations" should be replaced by 'univalent radii of cations'; and in line 3, Be^{3+} should be replaced by Be^{2+} .

17. On p. 556, line 4 from the bottom, CaCl should be replaced by KCl .

18. On p. 556, in line 3 from the bottom, it is written that "sulphides of the ammonium sulphide group are precipitated when the solutions are acidified". This cannot be correct as these sulphides are not precipitated in acid solutions, and with the exception of CoS and NiS they are soluble in acids.

While discussing the constitution of thiosulphates the authors have made no mention of the isomerism of thiosulphuric acid, which is now well known.

19. On p. 599, S_2Cl_2 is described wrongly as *light* yellow, while it should be *dark* yellow.

20. On p. 676 in line 19 and 20, in the formula showing resonance for nitric oxide, the single bonds should be replaced by double bonds.

21. On p. 700, under *Analogy with Chlorates*, it is stated that the chlorates and nitrates are isomorphous; and the entire para is devoted to explain the analogy between the two. It has been stated further that the recent work of Pauling indicates a fundamental similarity in their electronic structure.

All these are incorrect. Chlorates with pyramidal structure (bond angles 106°) cannot be isomorphous with nitrates having planar structure (bond angles 120°), though they may have closely similar properties. It is the carbonate radical which may be isomorphous with the nitrate, as they are isoelectronic and isosteric.

22. On p. 757, in line 4, antimony is stated to be quadrivalent in $\text{M}_2[\text{SbX}_6]$. Magnetic measurements have, however, shown them to be mixtures of ter- and quinquevalent antimony.

23. On p. 840, in the equation for the formation of hypoborate, KOBH_3 should be replaced by KOBH_2 .

24. On p. 841, the formula for hypoboric acid should $[\text{BOH}_2]\text{H}$ and not $[\text{BOH}_3]\text{H}$.

Considering, however, the volume of the book, the number of errors is large, but some of them are of a quite serious type and cannot be ignored.

P R.

OSMOTIC PRESSURE AND MOLECULAR WEIGHT OF SHELLAC

By SADHAN BASU

The nature of solvent-solute interaction has been studied from the measurements of osmotic pressure of dilute shellac solutions

Molecular weights of hard and soft resins have been calculated from the osmotic pressure data. They have been found to be in accord with the values previously obtained by other authors.

In a previous communication (Basu, *J. Indian Chem. Soc.*, 1947, **24**, 148) it has been shown from the measurements of viscosity that the shellac dissolves molecularly in so-called good solvents, but with polar solvents there is always some probability of solvent-solute interaction. In the present communication an attempt has been made to confirm the previous observations from osmotic pressure measurements. Further, the calculation of molecular weight has been made from osmotic pressure data, since it eliminates many of the complications encountered in previous methods. In this section measurements have been done with the constituents of shellac, namely, hard and soft resins, after separating them.*

The rise of osmotic pressure with concentration of high polymer solutions has been a subject of great interest in the present time and extensive work has been done on the solutions of proteins (Adair, *Proc. Roy. Soc.*, 1925, **A,108**, 627; Pauli and Fent, *Kolloid Z.*, 1934, **67**, 288; Sørensen, *Z. physiol. Chem.*, 1918, **103**, 15), cellulose derivatives (Duclaux, *J. chim. phys.*, 1931, **28**, 537; Obogi and Broda, *Kolloid Z.*, 1934, **69**, 172), rubber (Caspari, *J. Chem. Soc.*, 1914, **105**, 1239) and several synthetic polymers (Kemp and Peter, *Ind. Eng. Chem.*, 1941, **33**, 1926; Flory, *J. Chem. Phys.*, 1941, **9**, 660). An excessive increase of osmotic pressure with concentration has been observed in all the cases. If the osmotic pressure be expressed as a power-series in concentration of solute, we get

$$\pi = Ac_2 + Bc_2^2 + Cc_2^3 + \dots \quad (1)$$

where c_2 = concentration of polymer, π = osmotic pressure in atmosphere and A, B, C , etc. are constants. At extremely low dilution, the higher powers of concentration will become negligible, leaving only the expression containing up to the square terms in equation (1)

$$\pi = Ac_2 + Bc_2^2 \quad (2)$$

which may be written as

$$\pi/c_2 = A + Bc_2 \quad (3)$$

That is, the graph of π/c_2 against c_2 is a straight line with a slope equal to B and an intercept on π/c_2 axis equal to A .

The value of A is directly connected with the number of particles that are moving independently, i.e., the state of ideal dispersion and consequently with the molecular

* Shellac is known to be a mixture of two resins: (i) hard resin, which constitutes 70% of lac, is a solid, insoluble in ether, while (ii) soft resin, which constitutes about 30% of lac, is a semi-liquid at ordinary temperature and is soluble in ether.

weight M_2 of the dissolved unit. Thus in a dilute solution, where the dispersion is ideal, it is possible to calculate the molecular weight M_2 from Vant Hoff's relation

$$\lim_{c_2 \rightarrow 0} \frac{\pi}{c_2} = \frac{RT}{M_2} \quad \dots \quad (4)$$

where R = gas constant and T = absolute temperature.

Interpretation of coefficient B in the expression (3) is somewhat difficult. First attempt towards this direction was made by Ostwald (*Kolloid Z.*, 1929, **49**, 60) and afterwards thoroughly investigated by Haller (*ibid.*, 1931, **56**, 257), Adair (*loc. cit.*), Burk (*J. Biol. Chem.*, 1930, **87**, 237) and others. They traced the second term back to the swelling phenomenon, *i.e.*, to solvent-solute interaction; or, in other words, the term B may be interpreted as a contribution of the forces between the solvent and the solute.

EXPERIMENTAL

Measurement of osmotic pressure was made by static elevation method, a Herzog's osmotic cell being used for the purpose (Herzog, *Z. physikal. Chem.*, Bodenstein Festschrift, 1931, p. 239). The most difficult part in this experiment was the preparation of the membranes. Cellophane tubes were cut in the form of circular discs, washed thoroughly first with water and then with benzene-alcohol (1:1) mixture. These discs were then swollen in alcohol-water mixture (60:40) for 12 hours. They were then removed and placed in pure alcohol. In using the membranes with solvents other than ethyl alcohol, the membranes were removed from alcohol, treated successively with a mixture of alcohol and the desired solvent, gradually increasing the proportion of the latter in order to replace alcohol from the pores of the membranes and finally they were kept in the pure solvent.

The osmotic pressure, π , in atmosphere was calculated from the relation :

$$\pi = \frac{(h_{\text{obs}} - h_0)\rho}{1033}$$

where ρ = the density of the solute, h_{obs} = the observed equilibrium height in cm. and h_0 = the capillary correction. This correction factor had been determined by dipping the capillary in the solution and observing the rise of the solution in the capillary. This was found to be not more than 3 mm. in any case.

Best result is generally obtained with the membranes prepared by swelling cellophane P.T. 600. But since this was not available, ordinary cellophane paper tubes were used. The permeability of the cellophane tubes were low and it took 8 to 12 hours to attain equilibrium. Further, it was not possible to measure osmotic pressure with a variety of solvents using this membrane. The reproducibility of the results with hard resin was within 5 to 7%, while with soft resin it was 3 to 4%.

The range of accuracy in carefully conducted experiment was within 2% as verified with alcoholic solution of glycine.

Separation of hard and soft resins, the two constituents of lac, was effected by the following method: Powdered, dewaxed, lemon shellac (100 g., 100 mesh) was mixed with twice its amount of powdered, purified sand and extracted with ether in a soxhlet. The ether solution on evaporation left soft resin which was further extracted with petroleum ether to remove any wax. The residue was dissolved in minimum amount of alcohol, reprecipitated with ether, redissolved in alcohol, and then it was poured into warm water. The hard resin was taken out from water by drawing it into fibre and then dried.

The solvents used were purified and dried by usual methods. The preparation of the solutions was effected by the methods stated in the previous paper (Basu, *loc. cit.*).

The results of osmotic pressure measurements with hard resin solutions in different solvents are given in Tables I-V and the corresponding $\frac{\pi}{c_2} - c_2$ curves in Fig. 1.

TABLE I

n-Butyl alcohol.

c_2 (g./litre)	π (atm.)	π/c_2 (atm.l/g.)
0.1	0.001438	0.01438
0.3	0.004872	0.01624
0.4	0.007000	0.01750
0.6	0.011760	0.01960
0.8	0.017120	0.02140

TABLE II

Ethyl alcohol.

c_2 (g./litre)	π (atm.)	π/c_2 (atm.l/g.)
0.2	0.003176	0.01588
0.5	0.009050	0.01810
0.8	0.016496	0.02062
1.0	0.021700	0.02170

TABLE III

Water (5%) in acetone.

c_2 (g./litre)	π (atm.)	π/c_2 (atm.l/g.)
0.2	0.003740	0.01870
0.5	0.013010	0.02602
0.7	0.021280	0.03040
1.0	0.037300	0.03730

TABLE IV

Water (10%) in acetone.

c_2 (g./litre)	π (atm.)	π/c_2 (atm.l/g.)
0.1	0.001570	0.01570
0.3	0.006240	0.02080
0.5	0.012260	0.02452
0.8	0.024800	0.03100
1.0	0.035800	0.03580

TABLE V

Water (15%) in acetone

c_2 (g./litre)	π (atm.)	π/c_2 (atm.l/g.)
0.3	0.005790	0.01930
0.5	0.011810	0.02362
0.7	0.018844	0.02692
1.0	0.032800	0.03280

The results of osmotic pressure measurements with soft resin solution in different solvents are given in Tables VI to X and the curves in Fig. 2.

TABLE VI

n-Butyl alcohol.

c_2 (g./litre).	π (atm.).	π/c_2 (atm.l/g.).
0.1	0.005180	0.05180
0.2	0.010464	0.05232
0.3	0.015960	0.05320
0.5	0.027040	0.05408

TABLE VII

Ethyl alcohol.

c_2 (g./litre).	π (atm.).	π/c_2 (atm.l/g.).
0.2	0.010496	0.05248
0.3	0.015900	0.05300
0.4	0.021312	0.05328
0.5	0.027200	0.05440

TABLE VIII

Water (5%) in acetone.

c_2 (g./litre)	π (atm.).	π/c_2 (atm.l/g.).
0.1	0.005240	0.05240
0.2	0.010692	0.05348
0.4	0.022112	0.05528

TABLE IX

Water (10%) in acetone.

c_2 (g./litre).	π (atm.).	π/c_2 (atm.l/g.).
0.2	0.005220	0.05220
0.3	0.010640	0.05320
0.4	0.016260	0.05420

TABLE X

Water (15%) in acetone.

c_2 (g./litre).	π (atm.).	π/c_2 (atm.l/g.).
0.2	0.010600	0.05300
0.3	0.016176	0.05392
0.5	0.027800	0.05560

The values of B , i.e., the slope of the curves for different solvents for hard and soft resins are given in Table XI.

TABLE XI

Solvent.	B	
	Hard resin.	Soft resin.
<i>n</i> -Butyl alcohol	0.0093	0.0052
Ethyl alcohol	0.0074	0.0052
5% Water in acetone	0.0255	0.0108
10% Water in acetone	0.0244	0.0100
15% Water in acetone	0.0216	0.0098

The molecular weights for hard and soft resins as calculated from extrapolated

$\frac{\pi}{c_2} - c_2$ values for different solvents are given in Table XII.

TABLE XII

Solvent	Hard resin		Soft resin	
	$(\pi/c_2)_0$	M_2	$(\pi/c_2)_0$	M_2
<i>n</i> -Butyl alcohol	0.01348	1857.5	0.05120	481.2
Ethyl alcohol	0.01390	1801.0	0.05112	489.8
5% Water in acetone	0.01390	1801.0	0.05120	481.2
10% Water in acetone	0.01360	1841.1	0.05112	489.8
15% Water in acetone	0.01360	1841.1	0.05112	489.8

DISCUSSION

The departure from ideal behaviour in the $\pi/c_2 - c_2$ curve is generally ascribed to solvation, the dissolved particles carrying with them so much solvent that their effective concentration is reduced. Provided they are individually solvated, extrapolation to infinite dilution will eliminate this error. Even if association of the particles occurs, measurements in sufficiently dilute solution would be expected to permit an extrapolation to the unassociated state at infinite dilution.

The extent of the variation of $\pi/c_2 - c_2$ curve depends both on the nature of solvent and that of solute. An attempt to systematize this behaviour has been made by Schulze (*Z. physikal. Chem.*, 1937, **A**, 180, 1) who based his deductions on the fact that the osmotic pressure is independent of molecular weight in the region above 10% concentration. It is logical to make the further assumption, as was done by Ostwald (*loc. cit.*), that the contribution to osmotic pressure, which is independent of molecular weight, is also a factor at low concentration, and is not negligible in comparison with the Van't Hoff osmotic pressure term. Ostwald traced this effect back to swelling phenomena and used an osmotic pressure equation given by

$$\pi = Ac + Bc^n \quad \dots (5)$$

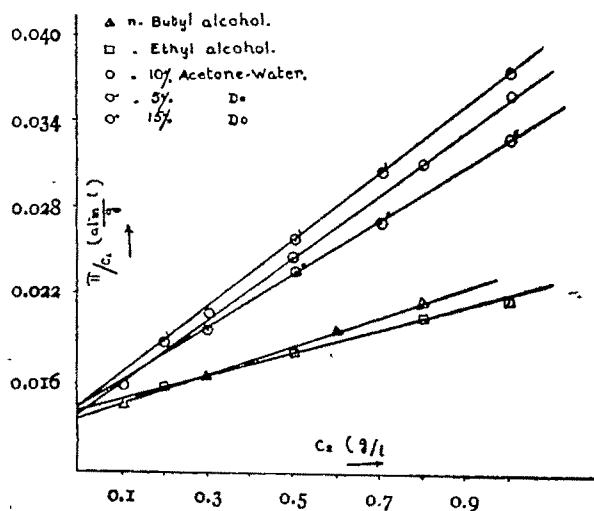
and found that n was usually nearly 2. Therefore, the term reduces to the same form as equation (3). Schulze, however, used a relation,

$$\frac{\pi}{c} = \frac{RT}{M} + \pi (K/\pi)^{1/\nu} \quad \dots (6)$$

This equation, however, demands that the deviation from ideality will be larger, the lower the molecular weight, while contrary is the case. Further, it has got a serious drawback that it requires solvation to become infinite at infinite dilution which is far from the case.

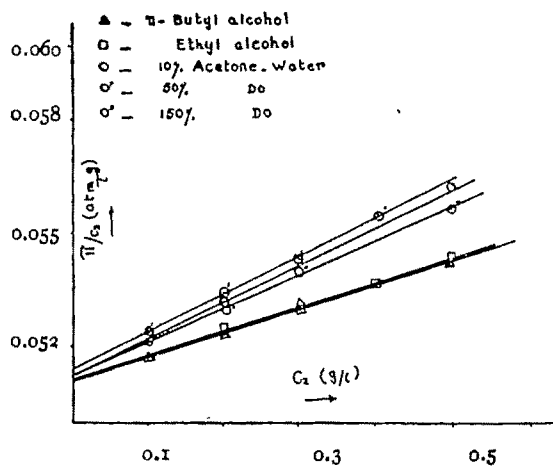
The values of B for hard and soft resins (Table XI) in *n*-butyl alcohol and ethyl alcohol are extremely small, though not zero. That is, in these solutions the osmotic pressure of the constituents of shellac is nearly proportional to the concentration. This fact suggests that the interaction of the dissolved particles with each other and also the energetic interaction with the solvent are less marked in these cases, confirming thereby our previous assumption that the shellac molecules are not solvated in these solutions. For acetone-water system, however, the values of B are much higher, most probably due to greater solvent-solute interaction, *i.e.*, solvation, the possibility of which has been noticed by Palit (*J. Indian Chem. Soc.*, 1943, **17**, 537). The values of B in acetone-water system, however, have been found to fall with increasing concentration of water. Since water is a non-solvent for shellac, it tends to precipitate shellac out of the solution as the concentration is increased, although up to a certain low concentration, water increases the solubility of shellac. As the particles tend to separate and agglomerate at higher concentrations of water, the interacting forces between the solvent and solute, and the solute and solute are gradually altered. Consequently, the values of B become difficult to be computed unless the various thermodynamic constants (*viz.*, heat capacity, chemical constant, ideal mixing, entropy, etc.) of these systems, while surrounded by molecules of its own species and also by molecules of different species, are known.

FIG. 1
Hard resin



In determining the molecular weights of the constituents of shellac in different solvents, namely acetic acid, dioxan, etc., the cryoscopic method has generally been used. But in this method the concentration of shellac should be sufficient to attain appreciable depression of freezing point and thus doubts have been expressed by several workers regarding the propriety of using this method on account of the possibility of association taking place in solution. Rast's

FIG. 2
Soft resin



method is also open to the objection as at the high temperature employed (176°) a part of resin may undergo polymerisation and the value actually obtained may not represent the true molecular weight of the original sample. In the osmotic pressure method all these difficulties and objections are absent since it uses a very low concentration and ordinary temperature.

From Table XII the molecular weights, calculated for hard and soft resins from osmotic pressure data in different solvents, appear to be fairly consistent though these values for molecular weight may not be obtained for all the samples, since an absolutely pure sample cannot be prepared by the methods available at present. These values may be compared with the values 1900-2000 obtained for hard resin and those of 513-556 obtained for soft resin by Palit and Bhattacharya (*J. Indian. Chem. Soc.*, 1939, 16, 258). For some samples, values found by these authors in case of hard resin varied from 1400 to 2000.

The author wishes to express his gratefulness to Dr. P.K. Bose, Director, Indian Lac Research Institute, Namkum, for his keen interest and constant encouragement in the present investigation.

PREPARATION OF 5 : 5-DIPHENYLHYDANTOIN

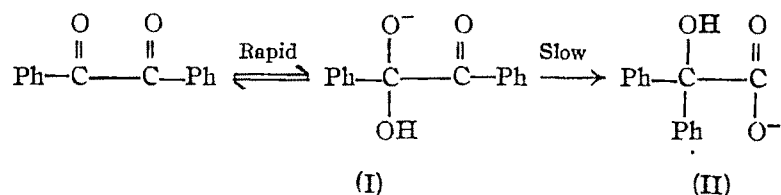
By J. SIKDAR AND T. N. GHOSH

An attempt has been made to explain the mechanism of the reaction in which benzil has been allowed to react with urea in presence of alkali to give rise to 5 : 5-diphenylhydantoin.

5 : 5-Diphenylhydantoin, first prepared by Biltz (*Ber.*, 1908, **41**, 1379) and later rejected as having relatively small hypnotic effect, has now found use in the form of its sodium salt as an anticonvulsant in the treatment of epilepsy (Putnam and Merritt, *Science*, 1937, **85**, 525).

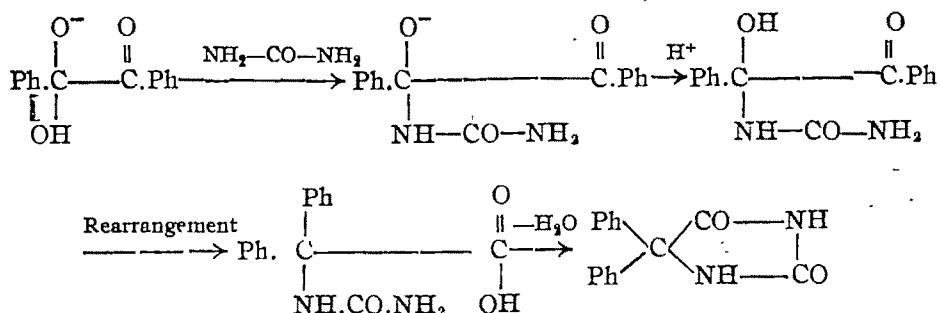
Hydantoin derivatives containing one or two substituents in position 5 are generally prepared from the cyanohydrin of an aldehyde or ketone containing the grouping $-\text{CO}_2\text{CH}_2-$ by the action of urea (Pinner, *Ber.*, 1887, **20**, 2351; 1888, **21**, 2320; 1889, **22**, 685) or ammonium carbonate (Bucherer and Steiner, *J. prakt. Chem.*, 1934, **ii**, **140**, 291). So far as the preparation of 5 : 5-diphenylhydantoin is concerned, the method due to Biltz (*loc. cit.*) has now been found to be more suitable than those described above. However, this method, which consists in treating benzil with alcoholic alkali and then heating the mixture with urea, has not been hitherto studied thoroughly with regard to the mechanism of the reaction involved. As is well known, benzil, when treated with alkali, undergoes molecular rearrangement to benzilic acid. It was therefore thought that in the method of Biltz, benzil was first converted into the alkali salt of benzilic acid, which then reacted with urea to yield the alkali salt of 5 : 5-diphenylhydantoin. But, curiously it has now been found that by heating under identical conditions the alkali salt of benzilic acid with urea in presence of alcohol, no reaction takes place.

With regard to benzilic acid rearrangement, Scheuing (*Ber.*, 1923, **56B**, 253) has shown that the potassium hydroxide addition compound of benzil forms within 2 to 3 minutes, whereas the rearrangement itself is a slow process. Ingold (*Ann. Repts. Chem. Soc.*, 1928, **25**, 124; 1933, **30**, 177) proposed the existence of an intermediate negative ion (I), produced by the addition of hydroxyl ion to benzil, and indicated the importance of an alkaline medium in the transformation. Subsequent investigation by Roberts and Urey (*J. Amer. Chem. Soc.*, 1938, **60**, 880) also indicates rapid, reversible addition of hydroxyl ion to benzil to form a negative ion (I), followed by a rearrangement.



In order to explain the formation of 5 : 5-diphenylhydantoin by treating benzil with alcoholic alkali and then heating the mixture with urea, and the non-reactivity of the alkali salt of benzilic acid towards urea in presence of alcohol (vide experimental),

it is now surmised that urea reacts with the intermediate negative ion (I) and the complex, thus formed, next isomerises to the form (II), ultimately forming 5 : 5-diphenylhydantoin by cyclisation :



The above mechanism of the reaction is supported by the following observations now made: (a) An alcoholic solution of benzil and urea, when heated, yields only diphenylacetylene-diureine (Angeli, *Ber.*, 1891, 24, 606; Anschütz and Geldermann, *Annalen*, 1891, 261, 129). (b) If a solution of benzil in alcoholic alkali is allowed to stand at room temperature (28-30°) for about 10 minutes (time sufficient for the formation of the intermediate negative ion) before urea is added and the resulting solution heated, 5 : 5-diphenylhydantoin and a trace of diphenylacetylene-diureine are formed. If the time allowed be even 10 hours instead of 10 minutes, the same reaction products are obtained and no benzilic acid has been isolated. (c) If a solution of benzil in alcoholic alkali is heated for only 15 minutes, cooled and treated with urea, and the resulting solution further heated, only benzilic acid is obtained and there is no formation of 5 : 5-diphenylhydantoin, furnishing thereby further evidence in support of the mechanism that urea reacts with the intermediate ion (I) and the complex, thus formed, next isomerises to form (II). These observations further show that alkali is essential for the transformation of benzil to benzilic acid and that, although the formation of the negative ion (I) is rapid (*cf.* Scheuing, *loc. cit.*), it does not undergo rearrangement at ordinary temperature (28-30°), though the rearrangement can be effected very rapidly at higher temperatures.

An attempt was made to isolate the compound (before it underwent rearrangement) formed by condensing urea with the intermediate negative ion (I). With this object in view, the reaction of benzil with urea in alcoholic alkali has been studied at ordinary temperature but isolation of unreacted benzil and a trace of diphenylacetylene-diureine shows that heat is necessary for this condensation and once the condensation takes place, the condensed product readily undergoes rearrangement and cyclisation under the influence of heat.

However, it has also been found now that under drastic condition, viz., by heating benzilic acid with urea at 135°-140°, 5 : 5-diphenylhydantoin is formed.

EXPERIMENTAL

Reaction of Benzil with Urea.—An alcoholic solution of benzil (7 g.) and urea (4 g.) was heated under reflux for 1½ hours. The reaction mixture was cooled and diluted

with a large volume of water. The solid obtained was filtered and extracted with hot alcohol. The alcoholic filtrate, on cooling, deposited a yellowish crystalline solid (2.5 g.) which was identified as unreacted benzil. The residue, insoluble in alcohol, was crystallised from glacial acetic acid in colourless, rectangular plates, m. p. 360° (decomp.), yield 2.8 g. Its identity with diphenylacetylene-diureine (Angeli, *loc. cit.*) was confirmed by mixed m.p. and a comparative study of the properties.

Reaction of Benzil with Urea in presence of alkali.—(i). The method of Biltz (*loc. cit.*) for the preparation of 5:5-diphenylhydantoin was tried under different conditions and in every case, besides 5:5-diphenylhydantoin, a small quantity of diphenylacetylene-diureine was formed. Biltz, however, did not mention anything about the formation of the latter compound in this particular reaction.

The best conditions under which 5:5-diphenylhydantoin is obtained in maximum yield with the least formation of diphenylacetylene-diureine and the method of separation of the latter compound from the former are given below.

Finely powdered benzil (15 g.) was added at room temperature to a cold solution of sodium hydroxide (7.5 g.) in water (38 c.c.) and alcohol (30 c.c.). After 10 minutes powdered urea (7.5 g.) was added with stirring and the mixture was then refluxed on the water-bath for $1\frac{1}{2}$ hours. The reaction mixture was cooled and diluted with a large volume of water, when a small quantity of a substance was found to remain insoluble. It was filtered, washed with water and was crystallised from glacial acetic acid in colourless, rectangular plates, m.p. 360° (decomp.), yield 0.7 g. Its identity with diphenylacetylene-diureine was confirmed.

The above filtrate (after separation of diphenylacetylene-diureine) was cooled in ice and then acidified with concentrated hydrochloric acid, when a solid was obtained which was filtered and washed with water, next with aqueous sodium bicarbonate and finally with water. It was crystallised from alcohol (charcoal) in colourless, rectangular plates, m.p. $294-96^{\circ}$ (decomp.), yield 11.5 g. (Found: N, 11.28. $C_{15}H_{12}O_2N_2$ requires N, 11.11 per cent). The above washing with aqueous sodium bicarbonate, on acidification under cooling, did not yield any solid, indicating thereby the absence of benzilic acid.

(ii). The above experiment was repeated only with the difference that the mixture of benzil, caustic soda and dilute alcohol was allowed to stay at room temperature ($28-30^{\circ}$) for 10 hours instead of 10 minutes, before urea was added and the mixture heated under reflux on the water-bath for $1\frac{1}{2}$ hours. In this case diphenylacetylene-diureine (3.5 g.) and 5:5-diphenylhydantoin (5 g.) were obtained and no benzilic acid could be isolated from the reaction mixture.

(iii). Powdered benzil (7.5 g.) was added at room temperature to a cold solution of sodium hydroxide (3.8 g.) in water (20 c.c.) and alcohol (15 c.c.), and the mixture was refluxed on the water-bath for 15 minutes, when a dark solution was obtained. The solution was cooled and urea (3.8 g.) was added. The mixture was again heated on the water-bath for $1\frac{1}{2}$ hours, cooled and then diluted with a large volume of water. The clear solution, on acidification under cooling with hydrochloric acid, yielded a solid which, after being thoroughly washed with water, was found to be completely soluble in aqueous sodium bicarbonate with effervescence. It was crystallised from boiling water (charcoal) in colourless, rectangular plates (6 g.), m.p. 150° . Its identity with benzilic

acid was confirmed by mixed m.p. with a genuine sample. Neither 5 : 5-diphenylhydantoin nor diphenylacetylene-diureine was obtained.

Attempts to condense Benzilic Acid with Urea.—(i). Benzilic acid (5 g.) was dissolved in cold sodium hydroxide (2.5 g. in 12 c.c. water) solution to which alcohol (9 c.c.) and urea (2.5 g.) were then added. The mixture was then heated on the water-bath for 1½ hours. The solution was cooled, diluted with water and then acidified with hydrochloric acid. The precipitate, thus obtained, was found to be completely soluble in aqueous sodium bicarbonate and after crystallisation from water it was proved to be unreacted benzilic acid, which showed that no reaction took place. Even when the conditions were varied, with the same reactants and solvents, no reaction took place.

(ii). An intimate mixture of benzilic acid (5 g.) and dry urea (2.5 g.) was heated in an oil-bath at 135°-140° for 6 hours. Ammonia and water vapour were found to evolve and the liquid melt gradually thickened. On cooling, a sticky mass, insoluble in water, was obtained, which was dissolved in cold dilute alkali and precipitated by hydrochloric acid. The solid was filtered, washed with water, next with aqueous sodium bicarbonate and finally with water, and was then crystallised from alcohol in colourless, rectangular plates (2.2 g.), m.p. 294-96° (decomp.). Its identity with 5 : 5-diphenylhydantoin was confirmed by mixed m.p. with the sample previously obtained and also by analysis.

BENGAL IMMUNITY RESEARCH LABORATORY,
CALCUTTA.

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STUDIES ON GUM JEOL (*ODINA WODIER*, ROXB.). PART III. THE ALDOBIONIC ACID

By S. N. MUKHERJEE AND S. C. CHAKRAVARTI

The jeolic acid isolated from gum jeol has been hydrolysed further by H_2SO_4 (conc. $\approx 1N$) and the aldobionic acid, so formed, has been further hydrolysed by prolonged refluxing with H_2SO_4 (conc. $> 1.5N$) and the products identified as *d*-galactose and galacturonic acid.

In Part II of this series (*J. Indian Chem. Soc.*, 1948, **25**, 63) it has been shown that the gum on mild hydrolysis yields some sugar and a complex acid which forms colloidal solution in water. This complex acid (termed "jeolic acid" in these investigations) has been further broken up by acids on continued refluxing to yield some more sugars. The sugars, thus obtained from hydrolysis of gum jeol, have been characterised as *l*-arabinose and *d*-galactose mainly.

Hydrolysis of the complex jeolic acid has been shown to yield, besides the sugar mentioned above, an acid which it is the aim of the present investigation to prepare in a pure state and characterise. Recent work on the constitution of the arabic acid from gum arabic has shown that it is a compound of glycuronic acid with *d*-galactose to which other carbohydrate groups remain bound by glycosidic binding (Butler and Cretcher, *J. Amer. Chem. Soc.*, 1929, **51**, 1519; Norman, *Biochem. J.*, 1929, **23**, 24, 524). In fact Weinmann (*Ber.*, 1929, **62**, 1639) evolved a complete method of preparing this *d*-glycuronic acid in considerable quantities from the gum and has thus lent support to the above views regarding its constitution. This acid kernel to which other carbohydrate groups are attached in the gum is looked upon by all these workers as galactose-glycuronic acid and it has been more thoroughly studied by Heidelberger and Kendall (*J. Biol. Chem.*, 1929, **84**, 629). Haworth (*Ber.*, 1932, **65**, 43) has shown that this acid kernel of the gum, commonly known as the aldobionic acid, is a compound of the reduced galactose group in position 6 with glycuronic acid (cf. Hotchkiss and Goebel, *J. Amer. Chem. Soc.* 1936, **58**, 358).

Work on a similar line has been taken up in the present case.

EXPERIMENTAL

Preparation of Calcium Aldobionate.—The method followed was essentially that of Heidelberger, Avery and Goebel (*J. Expt. Med.*, 1929, **49**, 847) with modifications in several stages wherever found essential.

About 200 g. of gum jeol, purified by precipitation with alcohol (*vide* Part I of this series, *this Journal*, 1948, **25**, 59) and dried in air, were directly dissolved in 2 litres of $N\text{-H}_2\text{SO}_4$ and refluxed for $\frac{1}{2}$ hour on the asbestos board. The concentration of H_2SO_4 and the period of refluxing were found to be sufficient for the hydrolysis of the gum to its

aldobionic acid stage, as it roughly produced the expected amount of reducing sugars (about 83%). After removal of H_2SO_4 quantitatively by $\text{Ba}(\text{OH})_2$, the solution obtained after filtration (deep yellow colour) was concentrated to about 300 c.c. under reduced pressure, when the colour deepened. It was then heated with CaCO_3 (to convert the acid, if any, into its Ca salt) and animal charcoal on the water-bath for $\frac{1}{2}$ hour and filtered. The colour still persisted. The solution was further concentrated to 100 c.c. whereby the colour became deeper. It was poured into 1000 c.c. of methyl alcohol (free from acetone) when a light yellow precipitate of the Ca salt separated out which was filtered. During filtration the precipitate turned brown and became sticky. Methyl alcohol was then removed from the Ca salt by heating it over an asbestos board on a low flame, when the precipitate changed to a spongy mass. About 18 g. of the crude calcium salt were thus obtained.

Purification.—The salt, thus obtained, was dissolved in water, boiled with animal charcoal, and filtered. The filtrate was poured into 10 times its volume of methyl alcohol and the precipitate filtered again. This process was repeated thrice when the salt showed no tendency to change its physical appearance as noted above. The yield on the dry basis was about 5.5 g. The colour of the aqueous solution of this salt was light yellow. Exactly 0.2052 g. of this Ca salt gave on analysis 0.0198 g. of CaO on ignition wherefrom Ca amounted to 5.8% of the original salt. Assuming the formation of a similar acid as the aldobionic acid from gum arabic by the combination of a molecule of hexuronic acid with a hexose and calculating for $(\text{C}_{12}\text{H}_{10}\text{O}_{12})_2\text{Ca}$, the percentage of Ca should be 5.33. The present salt thus shows a high percentage of Ca. On further purification the figure came down to 5.78% of Ca. This high percentage might also be due to the formation of some calcium uronate by further decomposition of the acid by hydrolysis (cf. Heidelberg, Avery and Goebel, *loc. cit.*).

The Cinchonidine Salt.—The above salt (5 g.), which was mostly Ca aldobionate, was treated with the theoretical amount of oxalic acid in solution and Ca oxalate was removed by filtration. The filtrate containing the free acid (aldobionic) was treated with alcoholic solution of cinchonidine containing just the equivalent amount of base in it. The alcohol was removed under reduced pressure. A small quantity of cinchonidine that remained behind was filtered off and the solution concentrated in *vacuo*. In the case of cinchonidine salt of aldobionic acid from gum arabic, Heidelberg and Kendall (*loc. cit.*) observed a spontaneous separation of the salt under similar conditions. This point was carefully observed in all the three different samples of the cinchonidine salt prepared in this connection but every time it was found that the cinchonidine salt, if formed, remained in solution and did not separate on concentration. This suggests that the cinchonidine salts, and therefore the aldobionic acids from the two gums, might be different from each other.

However, the concentrated solution of the cinchonidine salt was reddish in colour and fairly viscous. The solution was kept at 0° for about 3 days in a refrigerator but no crystal was found to separate out. The solution was then kept immersed in a freezing mixture when crystals were observed to come down in an hour's time. Attempt was made to separate these crystals by filtration in a funnel kept cool in the freezing mixture but crystals melted as soon as they approached the room temperature. Owing to such

difficulties crystallisation by acetone was tried but a gummy precipitate came down. This gummy mass was dissolved in water and allowed to crystallise but to no effect. Attempts at crystallisation of the cinchonidine salt were therefore abandoned and the solution was evaporated to dryness slowly under reduced pressure when an amorphous brown mass melting within $150-160^{\circ}$ was obtained (Heidelberger and Goebel, gives m. p. 172° , *J. Exp. Med.*, 1929, **49**, 854).

Isolation of the Acid.—The amorphous cinchonidine salt was dissolved in water and cinchonidine removed by treatment with baryta till neutral to phenolphthalein and filtered. Barium was then removed by H_2SO_4 quantitatively and the solution concentrated in *vacuo*. A slight flocculent mass was observed to come out on concentration; it was filtered off and the filtrate further concentrated in *vacuo* till the residue swelled up to a spongy mass. The residue was dissolved in minimum amount of water, and acetone added till turbidity was perceptible. No crystals were obtained.

This failure to obtain crystals of aldobionic acid or its cinchonidine salt by the same method, which was successful in the case of gum arabic, further suggests a fundamental difference between the acids obtained from the two gums.

It was therefore thought desirable to prepare the amorphous acid and then to purify the sample as far as practicable. Obviously it was found useless to proceed through the cinchonidine salt. The purified calcium salt (4 g.) from a previous operation, mentioned above, was quantitatively treated with oxalic acid to remove calcium. The aldobionic acid was then removed from the solution by evaporation to dryness in *vacuo*, the residue being extracted with 700 c.c. of methyl alcohol. The salt appeared to be sparingly soluble in methyl alcohol (cf. the corresponding acid derived from arabic acid). The methyl alcoholic solution was evaporated under reduced pressure to 100 c.c. when a white flocculent precipitate was obtained. The remaining solution after removal of this precipitate was concentrated in vacuum at the room temperature since the substance tended to charring at higher temperatures. When the solution was highly concentrated and presented a viscous appearance, solids began to make their appearance on the sides of the vessel. On further concentration needle-shaped crystals were obtained. But the crystals could not be recovered since, when the methyl alcohol was completely removed, the crystals turned into a spongy mass which could be easily broken and scraped out from the vessel. The amount obtained was 0.4 g. from 4 g. of Ca salt. It was orange in colour and if kept for some time, it turned sticky and brown in colour. After about 24 hours the mass became hard and brittle. The amorphous acid (0.3619 g.) was dissolved in 200 c.c. of water and its rotation observed in a dcm. tube amounted to $+0.18^{\circ}$. $[\alpha]_D^{25} = +99^{\circ}.45$. (Found: C, 40.40; H, 5.61; O, 53.90. $C_{12}H_{20}O_{12}$ requires C, 40.45; H, 5.62; O, 53.93 per cent).

Identification of the Aldobionic Acid.—The aldobionic acid, thus obtained, appears to have a formula $C_{12}H_{20}O_{12}$ which is identical with that obtained by Heidelberger *et al* (*loc.cit.*) from gum arabic, and which has been identified by them to be galactose-glycuronic acid. In the present case the acid obtained differs in many respects in point of solubility etc. from the latter and it appears that although they might have identical formula they are still fundamentally different. For this reason the present aldobionic acid was further

hydrolysed into its constituent acid and sugar, if there be any, and the constituents identified and characterised.

(i). *Uronic Acid*.—The impure aldobionic acid (5 g.), obtained by removal of Ca from the crude calcium aldobionate (5 g.) was refluxed with H_2SO_4 (about 1.5 N) for about 20 hours and the excess of H_2SO_4 removed by $\text{Ba}(\text{OH})_2$ quantitatively. The acid was then converted into its Ba salt by further addition of $\text{Ba}(\text{OH})_2$ till neutral by test with phenolphthalein. The solution was then poured into 5 times its volume of 98% alcohol when a white precipitate came down. The precipitate was filtered and was observed to change to a brown colour and became sticky on keeping. The filtrate still contained some Ba salt dispersed in solution which settled in about 72 hours at the room temperature (28-29°). The Ba salt thus collected was then purified by dissolution in minimum quantity of water and precipitation twice by alcohol. Ba was then quantitatively removed by H_2SO_4 and the filtrate obtained by separation of BaSO_4 was poured into twice its volume of alcohol. From analysis of an aliquot part of this solution necessary amount of cinchonidine, equivalent to the acid present, was added, and the solution evaporated in *vacuo* to about 7 or 8 c.c., when small needle-shaped crystals separated out. On keeping for 24 hours a good crop of crystals was obtained. Another crop was obtained by further concentration of the mother liquid after separating the first crop. The crystals obtained in two crops were then dissolved in absolute alcohol and boiled slowly on a water-bath with animal charcoal to remove the colour. After removal of charcoal by filtration sufficient water was added to render the concentration of alcohol 75% by volume. Needle-shaped crystals then began to appear in about 4 hours' time and a good amount was obtained after about 24 hours. The crystals were again dissolved in alcohol and recrystallised from 75% alcohol. Final yield was about 0.5 g. (about 10%).

The crystals, thus obtained, were believed to be of the cinchonidine salt of the hexuronic acid. It melted sharply at 224° (cinchonidine salt of glycuronic acid melts at 204° and that of the acid obtained from the similar salt from gum arabic melts at 198°, cf. Heidelberg *et al.*, *loc. cit.*). This suggests that the uronic acid obtained from gum jeol might be different from that of gum arabic.

This salt was hydrolysed by addition of $\text{Ba}(\text{OH})_2$ to separate the cinchonidine and to form a Ba salt which was subsequently treated with H_2SO_4 to remove all barium. After filtering off the BaSO_4 , the solution was evaporated to a small bulk under reduced pressure. A small quantity of the acid separating in the solid state was first tested with Tollen's reagent when a red coloration indicated the presence of uronic acid and/or a pentose sugar. The m.p. of the substance was observed to be 160.5° and its $[\alpha]_D^{20}$ (observed in 1% aqueous solution) was +57.2 (m.p. of *d*-galaurctonic acid is 159° and its $[\alpha]_D = +55.6$, vide Thorpe, "Dictionary of Applied Chemistry," Vol II, p. 297). (Found: C, 36.9; H, 5.2; O, 57.9. Calc. for *d*-galacturonic acid: C, 37.1; H, 5.15; O, 57.73 per cent).

The acid was then oxidised by HNO_3 (1:1) to convert it into a dibasic acid, if possible. The acid so obtained presented a crystalline appearance of mucic acid melting sharply at 216° (m.p. of mucic acid, 218°). It was further confirmed by converting it into the tetraacetyl derivative (vide Part II of this series, *loc. cit.*) which melted at 262° (m.p. of the tetraacetyl derivative of mucic acid, 266°). The dibasic acid was further confirmed by

a negative test (that it was not saccharic acid) by converting it into the potassium salt which was found to be soluble. An insoluble salt would have indicated the existence of saccharic acid. The uronic acid from the gum thus appears to be *d*-galacturonic acid (contrast the glycuronic acid obtained from gum arabic).

(ii). *The sugar*.—The filtrate, obtained after separation of the Ba salt of the hexuronic acid by alcohol contained some sugar as suspected from its reducing properties. The sugar was recovered by evaporation in *vacuo*. It was then taken up in a small amount of hot glacial acetic acid and filtered. The sugar crystallised on cooling and recrystallised twice from methyl alcohol. The yield was about 0.3 g.* The sugar was not a pentose as it did not respond to the furfural test. It was therefore believed to be a hexose and confirmed by combustion experiments. (Found: C, 39.8; H, 6.8; O, 53.4. Calc. for $C_6H_{12}O_6$: C, 40; H, 6.67; O, 53.3 per cent).

The sugar melted at 168° (m.p. of *d*-galactose, 166°) and showed a specific rotation, $[\alpha]_D^{28} = +82$, while $[\alpha]_D^{28}$ for *d*-galactose was found to be $+80^\circ$. The mixed melting point with *d*-galactose was observed to be sharply at 166° . Confirmatory tests were performed on the suspected *d*-galactose by conversion into its dibasic acid by treatment with HNO_3 (1:1). The crystals of the dibasic acid presented peculiarities of mucic acid in appearance and an almost identical m.p. of 214° . Further confirmation was made by converting the mucic acid into its tetraacetyl derivative and noting its m.p. (264°). The sugar thus definitely appears to be *d*-galactose,

CONCLUSIONS

Drastic hydrolysis of gum jeol with H_2SO_4 (about 1*N*) yields an aldobionic acid which has been isolated, purified and characterised.

The aldobionic acid decomposes on hydrolysis with H_2SO_4 (1.5 *N* approx.) and yields a hexuronic acid which has been identified with galacturonic acid and a sugar which has been confirmed to be *d*-galactose.

The aldobionic acid from gum jeol is thus galactose-galacturonic acid (cf. galactose-glycuronic acid from gum arabic).

The difference between gum arabic and gum jeol thus appears to be more fundamental than what it appears at the first sight. The differences in solubility or physical appearance are probably outward manifestations of an intrinsic difference of a more fundamental type. Gum jeol appears from the percentage of sugar obtained from it to be more complex than gum arabic. While the complex acid (jeolic acid) can be obtained from

* The same amount of aldobionic acid yielded about 0.5 g. of the hexuronic acid. Assuming that the aldobionic acid is formed by combination of hexuronic acid with a hexose in molecular proportion, 0.5 g. of the uronic acid would combine with 0.45 g. of hexose, 0.3 g., obtained above is thus too small but it may be due to the incomplete separation of the sugar.

gum jeol by mild hydrolysis with H_2SO_4 (0.5 N) that of gum arabic is more easily obtained by the mere removal of the basic radicals present in the gum (Part II of the series, *loc. cit.*). This aspect will be taken up again in the next part (Part IV) in connection with the electrodialysis of both the gum solutions.

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PHYSICAL CHEMISTRY LABORATORIES,
COLLEGE OF ENGINEERING AND TECHNOLOGY, JADAVPUR,
AND
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA.

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STUDIES IN BACTERIAL AMYLASES. PART I. EFFECT OF DIFFERENT FORMS OF NITROGEN ON THE FORMATION OF AMYLASE IN BACTERIA

BY BHAGWAN S. LULLA

Different sources of nitrogen in the formation of bacterial amylase employing the strain N.C.T.C., 2027 N (allied to *B. subtilis*) have been investigated. Among the sources of nitrogen tried, ammonium lactate has been found to be the best enzyme-former. Aeration has been found to augment the yield of amylase considerably.

Amylases constitute an industrially important and widely distributed group of enzymes. Among the various sources of amylase, bacteria constitute the best available source for the manufacture of the enzyme.

Bacterial amylases, which generally have a higher content of the liquefying fraction (α -amylase component) and which are capable of functioning at higher optimal temperatures and reactions, are eminently suited to be employed for the desizing of the textiles and other allied processes in textile industry.

A systematic enquiry was therefore directed towards elucidating the nutritional factors and the cultural conditions which influence the formation of amylase in certain types of bacteria in general, and in a particularly highly amylolytic strain of bacteria.

The effect of different forms of nitrogen on the formation of amylase in bacteria was investigated by several workers (Wallerstein, *Ind. Eng. Chem.*, 1939, **31**, 1218; Tilden and Hudson, *J. Amer. Chem. Soc.*, 1942, **64**, 2139; Beckord *et al.*, *Ind. Eng. Chem.*, 1945, **37**, 692; Peltier and Beckord, *J. Bact.*, 1945, **50**, 711; Hockenhull and Herbert, *J. Biochem.*, 1945, **39**, 102; Beckord *et al.*, *Ind. Eng. Chem.*, 1946, **38**, 232; *Arch. Biochem.*, 1946, **10**, 41). These workers generally used the organic and complex forms of nitrogen in the culture media using organisms of *subtilis*, *polymyxa*, *macerans* etc. groups in relation to the formation of bacterial amylases. Mostly the work was conducted with the extracts of proteinaceous materials, either of vegetable or animal origin, but in some cases organic forms of nitrogen, like peptone, etc. were employed.

The importance of the availability of a suitable form of nitrogen in the culture medium was emphasised by Boidin and Effront (U.S. Patent, 1,227,374; 1,225,525; 1937). Systematic work on the efficiency of different forms of nitrogen on the formation of amylase, employing one single organism, has been found to be lacking.

The present paper relates to investigations on the different sources of nitrogen in the formation of bacterial amylase employing the strain N.C.T.C., 2027 N, very much allied to *Bacillus subtilis*.

EXPERIMENTAL

Selection of the strain of Bacillus Subtilis.—About 30 different strains of *Bacillus subtilis* reported to possess diastogenic activity were obtained from the National Collection of Type Cultures, India. These strains were screened on nutrient agar medium, previously incorporated with 0.2% of soluble starch. The extent of their amylolytic

activities was determined qualitatively by flooding the screens with $N/200$ -iodine solution, when measurable, clear and unstained zones around each of the colonies were secured; the one which gave the highest clearance zone was selected for these investigations.

The organism carries the number N.C.T.C., 2027 N in the repository of the National Collection of Type Cultures, India.

Preparation of the Inoculum.—The inoculum was prepared by transferring a loop of the culture from a nutrient agar slant to a tube containing 5 ml. of nutrient broth; the tube was then incubated at 37° in a slanting position on a wooden rack. After 24 hours' incubation, the tube was centrifuged till all the bacterial cells settled at the bottom. The clear supernatant layer was poured out and the cells were repeatedly washed on the centrifuge with sterilized $N/15$ -phosphate solution and the bacterial residue was finally made up to 25 ml. with the phosphate solution; 0.5 ml. of this inoculum was used throughout these investigations.

Evaluation of Starch-liquefying Activity.—The liquefying power of the enzyme sample was determined by viscometric method. The reaction mixtures consisted of 15 ml. of the 2% starch solution, buffered to a p_H of 7.0 and 1.0 ml. of the enzyme preparation; the total volume of the reaction mixture was 16.0 ml. Each experiment was accompanied by a control in which boiled enzyme was used in place of the active one. Ostwald's viscometers, thoroughly cleaned and dried, were employed for all viscometric studies. The relative viscosity with distilled water at 40° corresponded to a gravitational flow of about 58 seconds. The capillaries of the viscosimeters were specially selected so that they could be used for the reaction mixtures whose initial viscosities were comparatively high with 2% starch solution; the instrument gave a flow of about 150 to 160 seconds at 40° .

Viscosity determinations were conducted at 40° in an electrically heated and controlled thermostat. Readings were taken at known intervals of time lasting for an hour.

The Unit of α -Amylase.—One enzyme unit* is defined as that quantity of the enzyme which, acting on a 2% solution of starch (B.D.H.) at p_H 7.0 and at 40° , will bring about a 25% reduction in viscosity in 90 minutes.

Determination of the Enzyme Units.—The reaction was carried out in an Ostwald's viscometer, maintaining strictly the conditions specified above. The percentage of reduction of viscosity was plotted against time and the time course curve of the reaction was drawn. The time taken for the 25% reduction in viscosity was read off from the curve so constructed.

If the time taken for 25% reduction is 15 minutes, the enzyme preparation would contain 6 units.

Enzyme units per c.c. of a given sample $= 90/t$, t being the time (in minutes) for 25% reduction in viscosity.

Effect of different forms of Nitrogen on the Formation of Amylase in Bacteria.—

In order to find out the effect of different forms of nitrogen in relation to the formation of amylase in bacteria, it was found necessary to study the effect of excluding or limiting

* This has been found to be a very convenient unit since we have rarely found the activity of samples investigated falling below one unit.

the supply of oxygen in the culture media. With this end in view, two different and independent sets of experiments were conducted:

- (a) Placing culture tubes vertically and in a slanting position (25°) so that the latter set of tubes received greater degree of aerobic condition.
- (b) Blowing in a current of sterilized air through the culture medium placed in a flask.

The culture media of the following composition were employed. The results obtained at room temperature (25° - 27°) are given in Table I.

TABLE I

* Basal media	...	1.0 ml.
Starch solution (2%)	...	2.5
Nitrogen source (ammonium lactate equivalent to 2.0 mg. level of nitrogen)	...	10
pH	...	7.0
Volume made up to	...	10.0

* One litre of distilled water contained 1.0 g. of KH_2PO_4 , 1.0 g. of K_2HPO_4 , 0.5 g. of NaCl , 0.1 g. of CaCl_2 , 0.1 g. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.01 g. of MnSO_4 and 0.01 g. of FeSO_4 .

The data in Table II reveal interesting facts:

- (a) The culture tubes, which by virtue of their being placed in a slanting position were exposed to a higher degree of aeration, formed in themselves very nearly 4 to 5 times as much of amylase as compared with the culture tubes in the vertical position, otherwise maintained under the same conditions. The vertically placed tubes had comparatively a very limited surface exposed to air. The results indicate the essential importance of aeration in the formation of amylase.
- (b) When air was blown through the culture media, there was a 25 to 30% increase in the concentration of the enzyme formed.

TABLE II

Effect of aerobic and anaerobic conditions on the formation of bacterial amylase.

(Figures given in enzyme units per 10 ml. of the medium).

Incubation period.	a		b	
	Vertical.	Slant.	Non-aerated.	Aerated
72 hrs.	20.8	100.5	116.2	165.2
96	24.3	114.5	134.3	188.0
120	30.7	131.2	148.8	186.0

All further experiments in this line were carried out under conditions of aeration. The method of culturing the bacteria in specially large tubes kept in a slanting position was uniformly adopted to facilitate adequate aeration of the cultures.

FIG. 1

Time course curve of enzyme extracts from cultures grown on different sources of N without aeration.

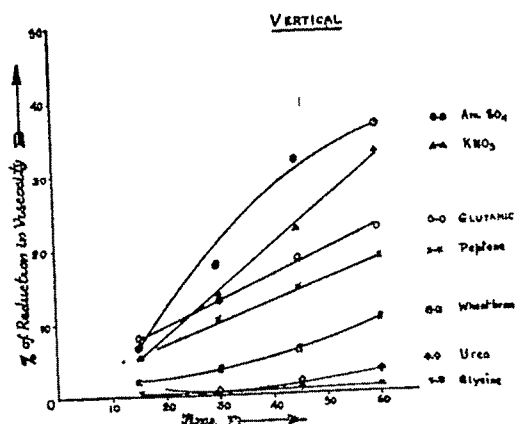
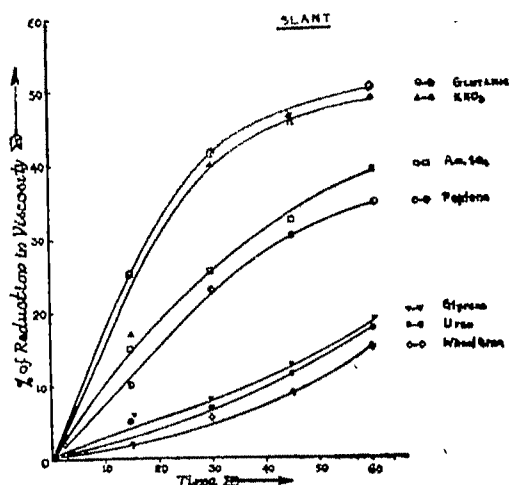


FIG. 2

Time course curve of enzyme extracts obtained from cultures grown on different source of N with aeration.



In some cases, the effect of aeration was also studied side by side with the nitrogen series. The nitrogen level in the culture media was tried mostly at two levels *e.g.* 1.0 mg. and 2.0 mg. The composition of the media for these studies was the same as previously described under the aeration studies, excepting that the source of nitrogen was variant. Incubation was carried out at 37° for 72 hours. After 72 hours' growth, toluene (2 ml.) was added to each of the tubes. These tubes were then incubated at 30° for 24 hours to effect autolysis of the cells. After this period, the tubes were cen-

trifuged at 3000 r.p.m., when a clear supernatant layer was obtained. The reaction curves obtained with different amylase preparations have been plotted (time-percentage of reduction in viscosity) and the enzyme units calculated from these curves have been tabulated (Figs. 1-4 and Tables III and IV).

TABLE III

Effect of aeration on the formation of diastase.

Nitrogen source (0.7 mg. level of nitrogen).	Enzyme units for 10 c.c. of the medium.*	
	Slant.	Vertical.
1. Glutamic acid	60.0	13.0
2. Glycine	12.6	Negligible
3. KNO ₃	50.0	18.0
4. Ammonium sulphate	32.0	23.0
5. Urea	11.69	Negligible
6. Peptone	26.00	10.6
7. Wheat bran extract (papain digest)	11.25	Negligible

* Wherever found necessary, the reaction curves were extrapolated to 25% reduction in viscosity and the corresponding time noted for the determination of the enzyme unit.

TABLE IV

Effect of different forms of inorganic nitrogen on diastase formation.

(Results expressed as units of enzyme per 10 c.c. of medium at 1 and 2 mg. levels of nitrogen).

Nitrogen source.	Nitrogen level	
	1.0 mg.	2.0 mg.
Ammonium lactate	70.0	112.5
Sodium nitrate	36.0	36.0
Potassium nitrate	33.3	34.0
Ammonium nitrate	...	48.6
Ammonium sulphate		
+sodium nitrate	40.0	44.0
Ammonium sulphate	Negligible*	Negligible *
Ammonium chloride	Do	Do

* Due to low p^H .

The following classes of compounds were investigated to ascertain the effect of the quality of nitrogen source on the formation of bacterial amylase.

(a) *Organic Forms of Nitrogen.*—Both the simpler and the more complex forms were tried as sources of nitrogen. Of the simpler organic forms of nitrogen employed, glutamic acid constituted the best source of nitrogen from the point of view of enzyme formation, while glycine gave very poor results. Wheat bran extract and peptone, both gave comparatively low results.

(b) *Inorganic Forms of Nitrogen*.—Principally two inorganic sources of nitrogen were tried, the ammonium salts and the nitrates. When ammonium salts were employed, the acidic anion residue accumulated resulting in a lowering of the p_n of the medium; with nitrates, however, the cation residue was left as a residue tending to raise the p_n of the medium. Ammonium nitrate was also tried with the expectation that both ions

FIG. 3

Effect of inorganic forms of N on the formation of diastase (2.0 mg. level).

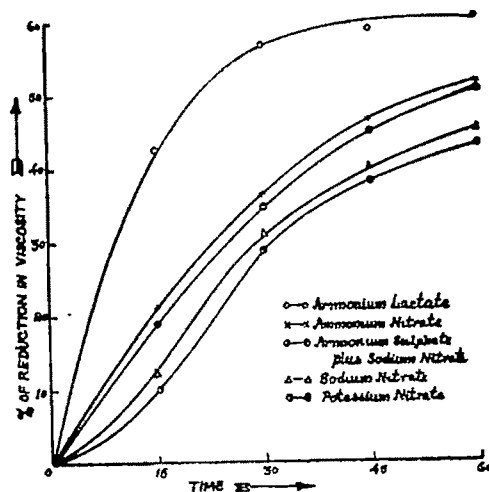
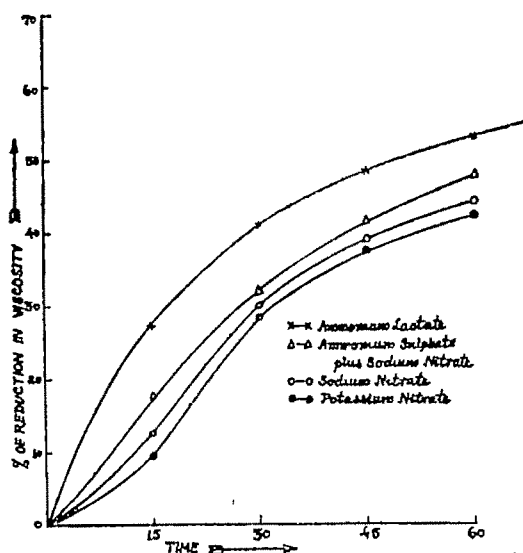


FIG. 4

Effect of inorganic forms of N on the formation of diastase (1.0 mg. level).



might be utilised at the same rate, leaving no residual effects. The mixture of the salts, ammonium sulphate and NaNO_3 , was tried with the expectation that the p_H of the medium after utilisation of the nitrogen bearing ions would remain constant due to the neutralisation of the equivalent residues.

When ammonium salts of inorganic acids were employed as the source of nitrogen, *e.g.* $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl , negligible quantities of diastase were formed. There was a fall in the p_H of the medium as it very often went down to 4.8 and the amylase, even if it were formed, would get continuously inactivated at this low p_H . In the case of nitrates, however, appreciable quantities of the enzyme were formed and the p_H rose often to a maximum of 7.6.

The best form of inorganic nitrogen appears to be ammonium lactate as evidenced by the high formation of amylase when the salt is furnished as the source of nitrogen. The p_H of the medium remains constant and possibly the lactic acid ion also contributes effectively towards the formation of the enzyme.

It was therefore of interest to study a series of the ammonium salts of a number of fatty acids to determine and evaluate the efficiency of the fatty acid moiety of the salt. The results of these studies are given in Table V.

TABLE V

Effect of ammonium salts of different fatty acids on the formation of diastase.

(Results expressed as units of enzyme per 10 c.c. of medium).

Nitrogen source.	Nitrogen level	
	1.0 mg.	2.0 mg.
Ammonium lactate	77.0	110.0
Ammonium citrate	58.5	104.0
Ammonium formate	.	35.5
Ammonium acetate	31.8	45.0
Ammonium propionate	22.5	7.03*
Ammonium butyrate	75.0	79.6
Ammonium gluconate	Negligible	Negligible

* Due to low p_H .

It appears from the table that the nature of the fatty acid associated with the ammonium salt determines the efficiency of ammonia as the source of nitrogen for diastase formation. Of the salts tried, ammonium lactate is the most efficient and the gluconate is the poor as enzyme formers.

In view of the pivotal position which lactic acid occupies in carbohydrate metabolism, it is not surprising that lactate should constitute the most efficient salt, as it may offer, in addition to the nitrogen, a highly reactive source of carbon, or carbon-containing group favouring the formation of diastase.

CONCLUSION

The formation of amylase in bacteria is influenced by the type of nitrogenous compounds supplied for its nutrition.

Of all the sources of nitrogen tried, ammonium lactate has been found to be one of the best enzyme formers; its excellence is to be attributed not merely to the ammonium ion but more to its exceptional combination with an easily assimilable intermediary of carbohydrate metabolism, i.e. the lactate. The salt is perhaps directly utilized without leaving any toxic or inhibitory residues. Among the simple organic forms of nitrogen investigated, glutamic acid offers the best source of nitrogen for the maximum yield of the enzyme.

Aeration is found to considerably enhance the yield of amylase.

The author is greatly indebted to Mr. M. Sreenivasaya for his valuable advice. Sincere thanks are also due to Sir J. C. Ghosh and Prof. V. Subrahmanyam for their kind interest during the progress of this work.

DEPARTMENT OF BIOCHEMISTRY,
INDIAN INSTITUTE OF SCIENCE,
BANGALORE.

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ELECTRONIC INTERPRETATION OF ORGANIC CHEMISTRY. EFFECT OF SUBSTITUENTS ON THE STRENGTH OF ORGANIC BASES

BY SANTI R. PALIT

It is suggested that the weakness of ammonia as a base arises out of the positive charge on its three hydrogen atoms which repels the approaching hydrogen-ion in the conventional base strength determination.

Any substitution of one or two hydrogens by alkyl groups increases the base strength since the repulsion factor is decreased. This is helped by the weak electron-donating (+I) nature of the alkyl groups which tends to increase the base strength by purely inductive way. The decrease of base strength on passing from a secondary to a tertiary base, is ascribed to steric factors. Based on this picture a consistent interpretation of the strength of all organic bases including the indicators is made.

The nature of the steric factor is analysed and shown to be composed of at least three independent effects. The first is the size and shape of the alkyl group; the second is the spatial interference by the methyl and of the alkyl chain with the free electron pair. The third is ascribed to a basic chemical fact, first hinted at by Pauling, that a N-C bond is inherently inferior to a N-H bond in its power of capturing a positive charge (here, H⁺ ion) owing to carbon being more electronegative than hydrogen.

It is shown that if the bases are compared against an uncharged acid like boron trialkyl, the order of the base strength should be different as the strong electrical effects are absent, and the experimental results so far available are found to be in agreement with what should be expected from the above viewpoint.

The effect of substituents on the strength of organic acids is fairly well understood from the electronic mechanism (cf. Dippy, *Chem. Rev.*, 1939, 26, 151; Branch and Calvin, "Theory of Organic Chemistry", 1945). A thorough discussion of base strength from a similar standpoint has never been attempted, though it is recognized in almost all current writings on the subject e.g., by Watson ("Modern Theories of Organic Chemistry", 2nd Ed., 1937), Pauling ("Nature of Chemical Bond", 2nd Ed., 1940), Wheland ("Theory of Resonance", 1944) and others, that the bases should in principle be subject to a similar treatment. However, a systematic discussion of base strength is met with great difficulty because even the similar bases behave rather anomalously. We cite below two examples to illustrate our point.

As opposed to the behaviour of acids, we should expect the base strength to decrease by the introduction of an electron-attracting (-I) group and to increase by the introduction of an electron-releasing (+I) group. However, the experimental values do not always support such conclusions and very irregular results are often obtained. For example, since alkyl groups are weakly electron-repelling in the order: propyl > ethyl > methyl in their purely inductive effect, we should expect the monoalkylamines to be

Previous two publications in this series are I. *J. Org. Chem.*, 1947, 12, 752; II. *J. Phys. Chem.*, 1947, 51, 837, and a very short note on the theme of the present publication, 1947, 51, 1028.

slightly stronger than ammonia in the above order. However, the experimentally observed order for the base strength of the monoalkylamines and ammonia is ethyl > *n*-propyl > methyl > ammonia, all the monoalkylamines being more than 25 times as strong as ammonia. The second anomalous point to note is that though the introduction of an alkyl group in ammonia increases its strength rather very strongly, the introduction of an alkyl group to a secondary amine to convert it into a tertiary amine depresses its strength considerably. Thus, ethylamine is about 30 times stronger than ammonia but triethylamine is only about half as strong as diethylamine.

Brown (*Science*, 1946, **103**, 385) has attempted to theorize on the subject based on experimental studies on the reaction between boron trialkyls and the amines. Brown (*J. Amer. Chem. Soc.*, 1945, **67**, 1452) rejects the thermodynamic dissociation constants of bases in aqueous solution as a measure of base strength attributing them as due to "complex solvation effects the importance of which cannot yet be estimated" and takes the strength of binding between a base and a boron trialkyl as a more correct measure of the base strength.

The purpose of the present paper is to suggest a new approach, based on classical concepts, which removes the apparent anomalies as mentioned above, and reconciles Brown's theory and his results with the question of base strength in aqueous solution.

The Problem of Base Strength of Ammonia

Since nitrogen is strongly electronegative, we should expect that the binding electron pairs in all N:H bonds in ammonia will be drawn closer to nitrogen away from the hydrogen atoms polarizing each N:H bond. As a result of this each of the three hydrogen atoms in ammonia will acquire a weak positive charge (Palmer, "Valency: Classical and Modern", 1944, pp. 132, 128; Pauling, *loc. cit.*). Any approaching hydrogen ion is attracted by the unshared pair of electrons but is repelled by the three positively charged hydrogen atoms round the nitrogen, as a result of which ammonia behaves as a weak base. However, if one or more of the hydrogens in ammonia are replaced by groups, the strength of the resulting base will depend on three factors:—

(i) The classical polar factors *i.e.*, the electron-donating (+I, or +T), or electron attracting (−I, −T) power* of the replacing groups.

(ii) The repulsion between the remaining hydrogen atoms round the central nitrogen atom and the approaching acid (here, the hydrogen-ion), which might be called the repulsion factor.

(iii) The availability of the unshared pair of electrons as influenced by the steric interference between the unshared pair of electrons and the alkyl group present round the central nitrogen atom.

This is the same as the classical "steric factor" and has been given a special name by Brown as B-strain.

* The notation of I and T effects and the nomenclature used in this paper are from Remick's "Electronic Interpretation of Organic Chemistry", John Wiley, 1943.

So, in simple compounds, where only the polar factor is operative or is too strong in comparison with the other factors, on substitution of any of the hydrogen atoms in ammonia by an electron-attracting group, a reduction of base strength will occur. Thus, hydroxylamines and hydrazine are found to be much weaker than ammonia (Table I). However, in most cases the phenomena will be complicated by the operation of the other factors and this will be discussed in what follows.

Alkyl Amines

The first factor which depends on the inductive effect is known to be very weak with alkyl groups, and hence can be neglected, or included along with the second factor whose effect is in the same sense, and so, the effects due to the second and the third factors need only be considered in the case of the aliphatic amines. These two effects generally act in opposite directions with the alkylamines, the first two factors tending to decrease it as we progressively replace the hydrogens of ammonia with alkyl group. For example, if a hydrogen atom in ammonia is replaced by an ethyl group, the second factor, which arises from the repulsion of the approaching hydrogen ion by the three positively charged hydrogen atoms in ammonia, will now tend to augment the strength. The approaching hydrogen-ion will now undergo repulsion only by two hydrogen atoms which are not symmetrically situated round its line of approach. This diminution of the repulsion to the approaching hydrogen-ion will cause an increase in the strength of the base in comparison to ammonia.

The second factor, which is a direct electrical repulsion effect, generally takes precedence and so ethylamine is found to be 30 times stronger than ammonia. The increment of strength, when we pass to diethylamine, is less (about 20 times) as the compensating steric factor is increasing. On passing to triethylamine, the steric factor is enough to compensate for the direct repulsion effect and actually a decrease in strength by a factor $\frac{1}{2}$ is observed. Hence, it appears that a balance between the two opposing factors is reached at the secondary amine which is therefore the strongest base in a given series of amines produced by successive replacement of the hydrogens in ammonia by a weakly inductive group. This behaviour seems to be characteristic of all alkylamines, as will be seen from Table I, where we always get a monotonic increase of strength up to the secondary amine, followed by a sharp drop in basicity on passing to the tertiary amine.

In comparing methylamines with ethylamines it is evident that all the above factors are operating in about the same way except that for the polar factors, methyl groups being less electron-donating (+I) than ethyl group. This accounts for the order: ethylamines > methylamines (Table I). On passing to propyl and butylamines, however, we should expect the strength to increase slightly but continuously, if the polar factor was only operative, but strong steric interference comes into play owing to the end of the long hydrocarbon chain approaching the lone electron pair, which more than compensates for the polar factor. This accounts for the order: ethylamines > propylamines or butylamines. This also elucidates the peculiar fact noted by various investigators "that the ethyl group is the most basilocious (base-producing) of all the alkyl groups" (Watson, *loc cit.*).

TABLE I

Dissociation constants of aliphatic amines (28°).

Base.	K_1 .	Ref.	Base.	K_b .	Ref.
Ammonia	1.79×10^{-6}	a	n-Propylamine	3.9×10^{-4}	c
Hydroxylamine	1.07×10^{-8}	b	Di-n-propylamine	8.2×10^{-4}	a
Hydrazine	1.5×10^{-6} (20°)	b	Tri-n-propylamine	4.5×10^{-4}	c
Methylamine	4.38×10^{-4}	a	n-Butylamine	4.09×10^{-4}	d
Dimethylamine	5.2×10^{-4}	a	Di-n-butylamine	2.05×10^{-3}	d
Trimethylamine	5.45×10^{-5}	a	Tri-n-butylamine	8.55×10^{-5}	d
Ethylamine	4.6×10^{-4}	c	isoButylamine	2.6×10^{-4}	c
Diethylamine	1.01×10^{-3}	c	Di-iso-butylamine	3.9×10^{-4}	c
Triethylamine	5.2×10^{-4}	c	Tri-iso-butylamine	2.1×10^{-4}	c

(a) Harned and Owen, *J. Amer. Chem. Soc.*, 1930, **52**, 5079.

(b) Landolt-Bornstein Tabellen, 5th Ed., 2nd Supplement, p. 1093

(c) International Critical Tables, Vol. VI, p. 259 (1929).

(d) Hall, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.

Peculiarity of the Methyl Group.—The methylamines are weaker than ethylamines not only because the methyl group is less electron-donating than the ethyl group, but also because the methyl group is itself a repellant for hydrogen-ion, as all the three hydrogen atoms become comparatively positive as a result of electron-drainage possibly owing to easy polarisability of the CH bonds in the methyl group. There is a pronounced relative retardation of strength at every step as we pass stepwise from ammonia to trimethylamine as compared to passing from ammonia to triethylamine. The author thinks that this peculiarity of the methyl group to behave as a weak positively charged centre and so, to be able to repel hydrogen-ion in comparison to other alkyl groups is considerably responsible for the above trend and a few other anomalies encountered with the methyl group.

It should be noted that neither the steric factor nor the direct repulsion should change uniformly with gradual replacement of the hydrogens in ammonia by alkyl groups. The repulsion factor of the three hydrogens is most affected by the first replacement, since the symmetrical disposition of the three centres of repulsion is destroyed and the remaining hydrogen atoms in the N-H bonds are less polarised, whereas the steric factor is the strongest at the third replacement, because this creates the maximum crowding of the big alkyl groups round the basic electron pair. This causes the increase of base strength in passing from ammonia to a primary amine and the decrease in passing from a secondary to a tertiary to be generally very large.

Mechanism of the Steric Factor

The mechanism of steric hindrance to the approaching hydrogen-ion by say the propyl group in propylamine, which makes it a weaker base than ethylamine, may not be pure space factor only, and an interesting suggestion made by Bennett and Moses (*J. Chem. Soc.*, 1935, 2364) and also by Dippy (*loc. cit.*) to explain the abnormally high

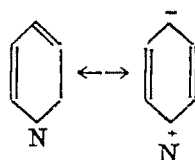
strength of butyric acid in comparison with the series of straight-chain fatty acids is well worth keeping in mind. It might well be possible that the mobility of the hydrocarbon chain causes its methyl end to come near to the unshared pair of electron to give an extra shielding effect.

We should like to point out another important factor, which is rather electrochemical in origin and often plays the most important role among all the possible factors which we have labelled together as 'steric'. Carbon being negative to hydrogen and N-C bond being less polarisable than a N-H bond, whenever a hydrogen atom of ammonia or an amine is replaced by an alkyl group, the new C-N bond reduces the receptive power of the nitrogen for an approaching hydrogen-ion tending to make the resulting base weaker. It is quite possible that this factor might be the chief cause of reducing the strength of an aliphatic tertiary amine in comparison with the corresponding secondary amine. However, we believe all the above factors, classed together as 'steric,' to operate and we need not single out any of them as the most important unless we have definite physical data to support our contention.

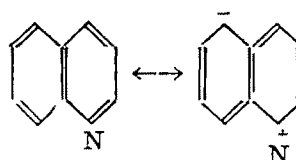
We would like to call this restrictive effect originating from the polar nature of the atoms by a special name and we propose the term "polar-striction effect". This idea of what we have called "polarstriction effect" is not wholly our own. A similar restrictive effect on the operation of resonance involving formal positive charges on nitrogen attached to a carbon has been postulated by Pauling (*loc. cit.*, p. 213) to explain the peculiar reduction of base strength of N-N'-dialkyl substituted guanidines. We believe this principle to be of wide applicability and shall see later how it causes the strength of an aromatic secondary base to increase on being converted into a tertiary one, as opposed to the behaviour of the aliphatic bases.

Cyclic Amines

According to the above considerations any compound, RNH_2 will be stronger than ammonia as long as R has only the electron-releasing or weak electron-attracting power. On the contrary, if R has a very strong electron-attracting power, the polar factor, which is no longer negligible, might more than compensate for the reduced repulsion effect. Since strong electron-drainage is a rule with resonance or tautomeric effect ($-T$), the very weak base strengths of aniline, pyrrole, pyridine and quinoline are easily understandable (Table II). This is, of course, the generally accepted opinion. With respect to pyridine and quinoline, the tautomeric effect, as shown below, is stronger in quinoline than in pyridine as it plays over a much longer conjugation and this makes quinoline weaker than pyridine.



Pyridine



Quinoline

In passing, it might be noted that the electron-drainage effect ($-T$) of the phenyl group is so strong that diphenylamine has practically no basic power. As soon as the strong electron-attracting power owing to the tautomeric ($-T$) effect in the above compounds is destroyed by reduction of the double bonds, the resulting compounds, *cyclohexylamine* and *piperidine*, become strong bases, much stronger than ammonia (Table II).

TABLE II
Dissociation constant of cyclic bases (25°).

Base.	Formula.	K_b .	Ref.
Aniline	$C_6H_5NH_2$	3.82×10^{-10}	a
Pyridine	C_5H_5N	1.71×10^{-9}	a
Quinoline	C_8H_7N	6.3×10^{-10}	a
Pyrrole	C_4H_4NH	ca. 10^{-10} or lower	b, c
<i>cyclohexylamine</i>	$C_6H_{11}NH_2$	4.39×10^{-4}	a
Piperidine	$C_5H_{10}NH$	1.25×10^{-3}	d
Pyrrolidine	C_4H_8NH	1.3×10^{-3}	

(a) Landolt—Bornstein, *Phsykalisch-Chemische Tabellen*, 5th Edition, 1936.
3rd Supplement, 3rd Part, p. 2121.

(d) Wheland, "Theory of Resonance," John Wiley, p. 178 (1944).

(c) Palmer, "Valency : Classical and Modern", Cambridge University Press, 1944.
p. 210.

(d) International Critical Tables, Vol. VI, p. 259 (1929)

N-Substituted Aromatic Bases

The substituted anilines show a slightly different behaviour from that of the alkyl amines. Since the extreme weakness of aniline is due to a resonance or tautomeric effect of the phenyl ring, the N-C bond will have a partial double bond character. Any substitution in the N- position by an alkyl group will tend to interfere with the above resonance or partial double bond character, because such a resonance tends to put a formal positive charge on the nitrogen atom which acts against the natural electronegativity of the N-C bond in the nitrogen—alkyl attachment. Hence, the resonance will fall off continuously as alkyl groups are progressively substituted in the N-position in aniline, which will therefore cause a progressive increase of base strength by such replacement. As a result, the strength continuously increases as each of the hydrogens is progressively replaced by alkyl groups. This accounts for the observed order: dialkylaniline > monoalkyl aniline > aniline (Table III). Further, as explained previously, we get the order: ethylanilines > methylanilines. Also, propyl groups have a stronger steric influence than ethyl groups and this accounts for the observed order : ethylanilines > propylanilines. Since resonance plays little or no part in the basicity of benzylamine, we shall expect it to have base strength similar to the aliphatic behaviour and not to aniline. These expectations are realised experimentally as will be observed in Table III that it is stronger than ammonia and its dimethyl derivative is weaker than the monomethyl derivative.

TABLE III

Base strength of N-substituted aromatic bases (25°).
 $(pK_{\text{H}} = -\log_{10} K_{\text{H}}/K_{\text{b}})$

Base.	pK_{H} .	Ref.	Base.	K_{b} .	Ref.
Aniline	4.62	<i>a</i>	Di- <i>n</i> -propylaniline	5.59	<i>a</i>
Methylaniline	4.85	<i>a</i>	Benzylamine	2.35×10^{-5}	<i>b</i>
Dimethylaniline	5.06	<i>a</i>	Methylbenzylamine	3.80×10^{-5}	<i>b</i>
Ethylaniline	5.11	<i>a</i>	Dimethylbenzylamine	8.5×10^{-6}	<i>c</i>
Diethylaniline	6.56	<i>a</i>	Ethylbenzylamine	4.75×10^{-5}	<i>b</i>
<i>n</i> -Propylaniline	5.02	<i>a</i>	Diethylbenzylamine	3.0×10^{-5}	<i>c</i>

(*a*) Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1922, 44, 3469.

(*b*) Carothers, Bickford and Hurwitz, *J. Amer. Chem. Soc.*, 1927, 49, 2908.

(*c*) International Critical Tables, Vol. VI, p. 260 (1929).

Nuclear-substituted Bases

If the substituted methyl group is introduced in the ring instead of in the N-position, it affects the base strength according to its position. In the *para* position, its strong electron-donation arising out of its hyper-conjugative effect is transmitted to the basic electron-pair across the ring to make the base much stronger. In the *meta* position, the electron-donation is very weak as no resonance can interplay and accordingly the base strength is very slightly increased. Hence, we should expect the order: *para* > *meta* > original base. This is the actually observed order with methylanilines as will be seen from Table IV.

It is very difficult to say anything with certainty about the *ortho* position owing to the well known unpredictable "*ortho*-effect", which here arises from at least two separate causes; one is the tautomeric effect of the ring and the other is the direct spatial interference by the group in the *ortho* position. In the case of a strong electron-attracting group ($-T$), such as the nitro group, both the above factors act in the same direction to reduce the strength and so, we get the order: *ortho* < original base. This is exemplified by the data for nitroanilines in Table IV.

TABLE IV

Base strength of nuclear-substituted aromatic bases (25°).

Original base.	Substituent	Position of the substituent.	pK_{H} .	K_{b}	Ref.
Aniline	None	—	4.62	5.7×10^{-10}	<i>a</i>
"	Methyl (CH_3)	Ortho	4.39		<i>a</i>
"	"	Meta	4.69		<i>a</i>
"	"	Para	5.12		<i>a</i>
"	Nitro (NO_2)	Ortho		5.6×10^{-15}	<i>b</i>
"	"	Meta		4.0×10^{-12}	<i>b</i>
"	"	Para		1.0×10^{-13}	<i>b</i>

TABLE IV (contd.)

Original base.	Substituent	Position of the substituent.	pK_n .	K_b	Ref.
Benzylamine	None	—		2.3×10^{-5}	c
„	Methyl (CH_3)	Ortho		1.70×10^{-5}	c
„	„	Meta		2.40×10^{-5}	c
„	„	Para		2.55×10^{-5}	c

(a) Hall and Sprinkle, *loc. cit.*

(d) Landolt-Bornstein Tables, 5th Ed., 2nd Supplement, p. 1093.

(c) Carothers, Bickford and Hurwitz, *loc. cit.*

Nuclear-substituted benzylamines behave exactly as discussed above in the case of aniline except that the interference owing to the *ortho*-effect is here stronger owing to the possibility of a six-membered ring formation.

Guanidine Bases

A direct consequence of our point of view is that compounds of the guanidine type, $(\text{NH}_2)_2\text{C}=\text{NH}$ should be very strong bases because all the factors which go to increase the base strength are very favourable. There is very little or no steric effect round the basic nitrogen atom ($=\text{NH}$) as it is connected by a double bond to the carbon atom. Also, the tautomeric effect, if it acts at all, will act in favour of the nitrogen atom in the $\text{C}=\text{N}$ bond making the nitrogen atom richer in electrons. All these factors contribute to make guanidines and amidines strong bases. An opposite state of affair exists in the ureas $(\text{NH}_2)_2\text{C}=\text{O}$ and amides $\text{R}.\text{CONH}_2$. The tautomeric flow of electrons owing to the $\text{C}\equiv\text{O}$ group is away from the nitrogen, which together make these compounds extremely weak bases.

Indicator Bases

The same considerations apply to indicator bases and it is possible to predict and interpret the change of indicator range with change of structure. Since the colour change of an indicator is due to the addition of a hydrogen-ion either to the indicator base or to the anion of the indicator acid acting as the base, we can apply the above considerations of base strength to all indicators. A stronger base requires less H-ion concentrations (higher p_n) in order to be converted into its conjugate acid: in other words, *the stronger an indicator base, the higher is its p_n range of colour change.*

The effect of alkyl groups can be exemplified with well-known indicators. For example, taking methyl orange and ethyl orange it follows from our foregoing discussions that the ethyl compound will be a stronger base. We should therefore expect ethyl orange to require less H-ion concentration (higher p_n) to convert it into its acid form, which is experimentally found to be true (Table V).

It should be noted that the basic atom in the common indicators is either the negatively-charged oxygen (as in phthaleins) or the neutral nitrogen (as in the azo indicators). Evidently, it will be easier to add a H-ion to a negatively charged oxygen than to a

neutral nitrogen. Hence, we find that the indicator ranges of phthaleines are generally in the alkaline side, whereas the azo indicators occupy the acid region.

It will also be observed that when a carboxylate is converted into a sulphonate (as for example, compare phenolphthalein and phenol red, or *o*-cresolphthalein and cresol red), the latter has a lower p_H i. e., it is a weaker base. This is easily understandable as we should expect a sulphonate ion to be more electron-attracting than a carboxylate ion, the former thus reducing the availability of the basic electron-pair.

The substitution of a methyl group in a phenolate-type base is free from '*ortho*-effect' and increases the base strength as is seen from the fact that cresols including *ortho*-cresols are stronger bases (weaker acids) than phenol. Probably, the strong electrical attraction between the negatively charged base and the phenol overcomes the disturbing *ortho*-effect. In conformity with this, the indicators, which are *ortho*-cresol derivatives, have a definitely higher p_H range than the similar ones derived from phenol (see Table V, data for 5 and 6, 7 and 8, and 9 & 10).

TABLE V

Colour change interval of indicators.

No.	Common name	Scientific name.	Trans-formation interval, p_H	Ref.
1	Methyl orange	Sodium dimethylaminoazobenzene sulphonate	3.1—4.4	b a
2	Ethyl orange	Sodium diethylaminoazobenzene sulphonate	3.5—4.5	b a
3	Methyl red	Dimethylaminoazobenzene carboxylic acid	4.3—6.3	a
4	Propyl red	Dipropylaminoazobenzene carboxylic acid	4.6—6.6	b
5	Phenolphthalein		8.0—9.8	b
6	<i>o</i> -Cresolphthalein	<i>o</i> -Methyl derivative of No. 5	8.2—9.8	,,
7	Phenolbenzein (Aurin, rosolic acid)	Benzoic acid analogue of No. 5	6.0—7.6	,,
8	<i>o</i> -Cresolbenzein	<i>o</i> -Methyl derivative of No. 7	7.2—8.6	,,
9	Phenol red	Phenol sulphonphthalein	6.4—8.2	,,
10	Cresol red	<i>o</i> -Cresolsulphonphthalein	7.0—8.8	,,
11	Chlorophenol red	Dichloro derivative of No. 9	4.8—6.4	,,
12	Bromophenol blue	Tetrabromo derivative of No. 9	3.0—4.6	,,
13	Bromocresol purple	Dibromo derivative of No. 10	7.0—8.8	,,
14	Dibromo- <i>o</i> -cresolbenzein	Dibromo derivative of No. 8	5.2—6.8	,,
15	<i>m</i> -Nitrophenol		6.5—8.5	,,
16	<i>p</i> -Nitrophenol		3.0—7.6	,,

TABLE V (contd.)

No	Common name.	Transformation interval, p_H .	Ref.
17	2 : 4-Dinitrophenol	2.0—4.7	b
18	2 : 5-Dinitrophenol	4.0—6.0	„
19	2 : 6-Dinitrophenol	1.7—4.4	„
20	2 : 4 : 6-Trinitrophenol	0.1—0.8	a
(a)	Table of Hydrogen Ion Concentration Ranges (p_H) and Color Changes, Eastman Organic Chemicals Co.		
(b)	Kolthoff, "Acid-base Indicators," translated by Rosenblum, Mollilen Co (1937).		

The halogen substituted sulphonphthaleins behave as expected. In accordance with the fact that halogen substitution in the ring depresses the base strength considerably owing to simple inductive effect, all the chloro-, bromo- and iodo-sulphonphthaleins have their colour range at a much lower p_H than the parent compound.

Exactly similar considerations apply to the nitrophenol. The introduction of a nitro group into phenol will diminish the base strength and hence the nitrophenols should be weaker bases than phenol which is experimentally found to be true. Of the two nitrophenols, *meta* and *para*, the *para* will be the weaker owing to the tautomeric or resonance effect and in agreement with this, the colour change interval of *meta* is found to be at a higher p_H . The dinitrophenols (2: 4, 2: 5 and 2: 6) should be weaker bases than mononitrophenols and so they should have a lower p_H range. Further, the *diortho* (2: 4) compound is found to have a lower p_H range which is evidently due to the *ortho*-effect referred to. The trinitrophenols are expected to have a p_H range further lower down and it is observed that picric acid (2: 4: 6- trinitrophenol) changes colour at a very strongly acid region. The above are only illustrative examples, and various other indicators can be similarly treated to obtain a good correlation among them.

A very serious discrepancy between the expectations of our theory and reported data has been noticed. Bader in 1890 reported the values for the acid dissociation constants of cresols to be of the order of 10^{-8} and that of phenol of the order of 10^{-10} . Later measurements have confirmed the correct order of the data for phenol but no precise measurement of the value for cresol seems to have been carried out except by Boyd by hydrolytic method which is generally considered not too reliable. Boyd reports values of the order of 10^{-11} , which is in agreement with what we should expect. If Bader's data are correct, it seems that a methyl group can increase the acid dissociation constant i. e., decrease the basic dissociation constant by a factor of 100. This seems to be very unusual and even opposite in sense to the expected direction of change. The matter evidently needs further careful experimentation.

Bases against Generalized Acids

If the approaching acid is not the positively charged hydrogen-ion, but a neutral molecule, e. g., a boron trialkyl, the powerful electrical forces arising out of the charged hydrogen-ion become practically absent and the other factors begin to assume importance.

The base strength will be mainly dependent on the availability of the unshared pair but other factors, such as weaker electrical forces and steric factors should also play an important part. The success of Brown's theory lies in the interpretation of the base strength considered from the last standpoint, particularly as depending on the size of the groups around boron and nitrogen.

The main experimental finding of Brown is that the relative strength of the bases NH_3 , RNH_2 , R_2NH , and R_3N , measured against any acid BR'_3 , depends on the size of the R and R', and with increasing size of R and R', the order tends to become from one extreme $\text{NH}_3 < \text{RNH}_2 < \text{R}_2\text{NH} < \text{R}_3\text{N}$ (called A order), to the other extreme $\text{NH}_3 > \text{RNH}_2 > \text{R}_2\text{NH} > \text{R}_3\text{N}$ (called F order). All intermediate orders between A and F exist (A order has actually not been found so far) depending on the size of R and R' and they are designated as B, C, D and E. Brown finds, for example, that with the same acid, boron trimethyl, as we pass along methyl, ethyl, isopropyl and *ter*-butyl amines the order changes to B, D, E and F respectively.

Evidently, such a behaviour can be explained by any two opposing factors one of which would tend to increase the strength giving rise to the A order and the other to decrease the strength producing the F order as the hydrogen atoms in ammonia are successively replaced by alkyl groups. Since increasing the size of R and R' groups always tends to shift the relative base strength curve to a higher order, Brown unerringly identifies the latter factor as of steric origin, depending on the size of the alkyl groups which introduces a kind of strain in the acid and base molecules and also at the "interface" of their union. Brown suggests the first factor to be the classical polar factor which by acting in opposition with the steric factor, produces the observed order.

This straightforward and simple theory of Brown is capable of accounting for the observed factors. Our ideas in aqueous solution are also in agreement with this theory, and it is of interest to note that the order of the values is mutually consistent. For example, since the repulsion factor plays a minor role in the case of generalized acids and the polar factor of the alkyl group is rather weak, we should expect that the ratio of strengths between ammonia and any base, *e.g.* trimethylamine, when compared against any uncharged acid *e.g.*, triethyl boron, will be greater than the same ratio with hydrogen-ion as the reference acid. The least value recorded by Brown (*J. Amer. Chem. Soc.*, 1946, **67**, 378) for the ratio of their dissociation constants against triethyl boron is $K_{\text{NH}_3} : K_{(\text{CH}_3)_3\text{B}}$ equal to $0.91 : 0.09 = 10.1$, whereas the ratio of their dissociation constants in water is about $1.79 : 5.45 = 0.33$. This shows clearly the importance of the charge of the acid against which the bases are compared and lends support to the bold assertion by Lewis (*J. Franklin Inst.*, 1938, **226**, 293) of the non-existence of any monotonic series of base strength. In a recent book, Luder and Zuffanti "(Electronic Theory of Acids and Bases", McGraw Hill, 1946) have discussed the question from various angles. Trimethyl boron, if used in the above example as reference acid, behaves somewhat anomalously owing possibly to the anomalous nature of the methyl group, as referred to earlier.

We consider the general outline of Brown's theory to be substantially correct but would think that included in his steric factor is also the 'polarstriction effect' we have discussed before. This effect becomes particularly important as we proceed from a secondary to a tertiary amine. The tertiary amine has no hydrogen attached to the

nitrogen atom and so it has very much less tendency than a secondary amine to combine with a boron trialkyl, as such combination involves a formal positive charge on the nitrogen. We believe that this is the main reason for the fact observed by Brown that the tertiary amine is invariably weaker than the secondary amine though the relative strength of the other amines varies with the nature of the alkyl group.

A limitation of Brown's theory is that though it predicts the tendency towards change of the type of curve for a series of amines with change in the alkyl group, it is unable to compare the strength of any two amines against any acid. For example, this theory cannot say which of the two bases between trimethylamine and triethylamine is stronger. The only thing it definitely says is that ethylamines should have a higher order curve than the methylamines. This limitation will probably disappear when we know more about the steric factors in the alkyl groups to which Brown's important results have drawn our attention.

DEPARTMENT OF PHYSICAL CHEMISTRY,
INDIAN ASSOCIATION FOR THE CULTIVATION
OF SCIENCE, CALCUTTA 12.

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CRYSTALLINE COMPONENTS OF THE SEEDS OF *HERACLEUM NEPALENSE*
(N. O. UMBELLIFEREAE). PART I *

BY CHANDRANATH BHAR

Six crystalline components have been isolated from the seeds of *Heracleum nepalense*. The first component of m p 188-89° is found identical with bergapten. The second component having m p 157-58° and mol. formula $C_{12}H_{18}O_4$ is isomeric with bergapten. The third component melts at 120-24° and possesses properties and structure identical with byakangelicin. The fourth component melting at 204° is found identical with allo-imperatorin. The other two components melt respectively at 202°-204° and at 231°.

H. Nepalense (N. O. *Umbellifereae*) is a small shrubby plant growing in the region of Nepal and extended to Bhutan at an altitude of 5000 to 12000 feet. It flowers early in September after which it gradually withers away. The seeds† were collected from the district of Darjeeling.

The dry crushed seeds have been extracted with ether in a soxhlet and from the ethereal extract five neutral crystalline compounds and an acidic crystalline substance have been isolated :

(i) A colourless compound (m. p. 188-89°) crystallising in long, silky needles has been isolated in 0.025—0.030% yield. It does not contain any phenolic OH group and it apparently behaves like a coumarin.

The analytical data are in agreement with the formula $C_{11}H_8O_3$ (OMe). The molecular weight by titration, has been found to be 218.6, agreeing with the formula, $C_{12}H_8O_4$ (216). The properties of the compound, as also the observed analytical values resemble those of bergapten (5-methoxy-furo-2': 3': 7: 6-coumarin), m. p. 191-92° (mixed m. p. with authentic sample same).

(ii) The second compound (m. p. 157-58°) crystallising in colourless needles, has been isolated in 0.015% yield. Phenolic hydroxyl appears to be absent. It behaves like a coumarin.

The C-H values and the methoxyl estimation agree with the formula, $C_{12}H_8O_4$ and hence it is isomeric with bergapten. It is, however, remarkable to note that the substance is transformed into bergapten when refluxed with alcoholic potassium hydroxide in a water-bath for 1 hour. Probably the compound is a stereoisomer of bergapten.

(iii) The third component, forming light yellow shining flakes (m. p. 120-24°), has been isolated in a fairly good yield, being 0.10% of the weight of the dry seeds.

A close inspection of the properties (vide experimental) of the compound suggests the presence of a coumarin nucleus. Analytical data are in agreement with the formula, $C_{17}H_{18}O_7$. Although it does not respond to ferric reaction, it contains two hydroxyl groups as it readily gives a diacetyl derivative. One methoxyl group is also present. Hence the compound may be written as $C_{16}H_{15}O_4(OH)_2(OCH_3)$. We have now to account for the remaining four oxygen atoms. If the substance under investigation is a furo-coumarin, three oxygen atoms may be accounted for. It occurred to us that the remaining oxygen atom might be present as an oxy-alkylenated group.

Späth and co-workers (*Ber.*, 1933, **66B**, 914) have shown that the ether linkage in the oxy-alkylenated coumarins can be cleaved by the action of concentrated sulphuric

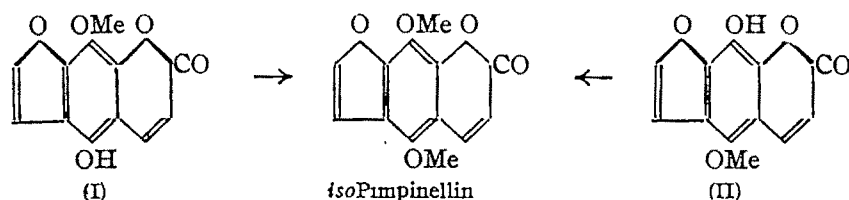
* A note was published in the '*Science and Culture*,' 1947, 12, 504.

† Kindly supplied to us by Messrs. G. Ghosh and Co.

and glacial acetic acids when the phenyl complex is eliminated creating a phenolic hydroxyl group in place of ethereal oxygen. When the above compound is heated with acetic-sulphuric acid mixture, a phenol (m. p. 218-19°) is obtained.

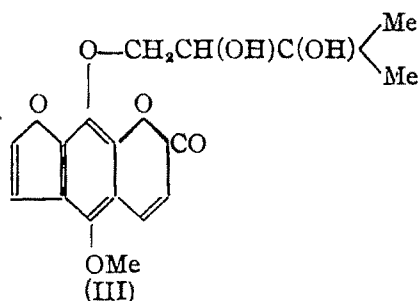
The analytical data of the phenol (m. p. 219°) agree with the molecular formula, $C_{12}H_8O_5$, and it contains one methoxyl group. On methylation it furnishes a dimethyl ether (m. p. 149°). If the phenol is a hydroxy derivative of a furo-coumarin, we can account for all the oxygen atoms. A search for the melting points of the derivatives of the known hydroxy furo-coumarins showed that the melting points of the dimethyl ether of the phenol and of isopimpinellin (Wessely and Kallab, *Monats.*, 1932, **59**, 161) were identical. The identity has finally been established by a direct comparison of the two compounds.

The isolation of isopimpinellin from the phenol conclusively proves that the phenol is a furo-coumarin, and since it contains a methoxy group and a free phenolic hydroxyl group, it is either (I) or (II).



The degradation of the compound to a phenolic substance which forms isopimpinellin by methylation leaves no doubt that the compound under investigation is a furo-coumarin derivative.

A search of the literature revealed a furo-coumarin, byakangelicin, isolated from the root of *Angelica glabra*, Makino (Japanese drug 'Byakusi') by Noguti and Kawanami (*Ber.*, 1938, **71B**, 344, 1428) (cf. also Bose and Chaudhuri, *Ann. Biochem. Expt. Med.*, 1946, **6**, 1) having the same molecular formula $C_{17}H_{14}O_7$ and almost identical m. p. 125-26°. Byakangelicin has been assigned the formula (III) and it seems probable to us that our furo-coumarin from the seeds of *H. nepalense* is identical with byakangelicin.



The properties and the reactions of our product are found to be similar to those of byakangelicin. The crystallised product $C_{17}H_{14}O_7$, H_2O from ethyl acetate, benzene or alcohol melts at 120-24° (lit. m. p. 117-19°), but when dried over P_2O_5 in vacuum at 110° for 8 hours, it melts at 124-26°.

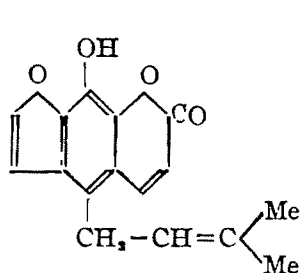
The derivatives of our product appear to be identical with those of byakangelicin

as shown below. Direct comparison of our substances with byakangelicin and its derivatives has not been possible in the absence of authentic specimens.

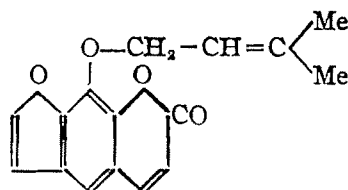
Derivatives.	Comp, m. p. 120-24° $C_{17}H_{18}O_7, H_2O$ m. p. 112°	Byakangelicin $C_{17}H_{18}O_7, H_2O$ m. p. 118-19°
Diacetate		
Phenol obtained by glacial acetic acid and sulphuric acid	218-19°	212°.

(vi) The fourth component, forming dull yellow shining plates (m. p. 229°) has been isolated in 0.04% yield. It is neutral to litmus, soluble in cold dilute alkali and does not respond towards ferric chloride. The substance is soluble in cold concentrated sulphuric acid with a permanent deep yellow colour. Thus the compound seems to be a coumarin.

Analytical values agree with the formula $C_{16}H_{14}O_4$. It contains one free phenolic hydroxyl group as it furnishes a light yellow monoacetyl derivative (m. p. 137°) and a monomethyl ether (m. p. 113°). Methoxyl group is absent. A study of its properties reveals similarity with allo-imperatorin (IV), m. p. 233°, which has been obtained by Späth (*Ber.*, 1933, **66B**, 1137) by distillation of imperatorin (V) at a pressure of 0.5 mm. of Hg.



(IV) Allo-imperatorin



(V) Imperatorin

It may be noted in this connection that allo-imperatorin was obtained synthetically by Späth and co-workers, and it has for the first time been isolated from a natural source. A direct comparison of m. p. and mixed m. p. with an authentic sample of allo-imperatorin and also the mixed m. p. of the methyl ether with an authentic sample of the methyl ether of allo-imperatorin establishes its identity with allo-imperatorin.

Product isolated	Synthetic product	
m. p. 228-29°	m. p. 229°	mixed m. p. 229°
Methyl ether, m. p. 113°	m. p. 113°.5	mixed m. p. 113°

The constitution of the remaining two components, (i) m. p. 202-204° and (ii) m. p. 231° still remains to be determined.

EXPERIMENTAL

The dried and powdered seeds (2.2 kg.) were extracted in a soxhlet with ether (16 hours). The deep green extract, which appeared to be brown in the transmitted light, was freed from the solvent by distillation. The oily residue deposited a light yellow solid on keeping overnight. The whole mass was then treated with benzene (200 c. c.), shaken well and filtered in a pump. Much difficulty was experienced during filtration as the oily product was originally contaminated with some water. The yellow residue

(A) was washed several times with benzene to remove associated oils and the filtrate (B) was collected. The following six constituents have been isolated :

(i) *Purification of the residue (A) : Isolation of Bergapten.*—The yellow residue (A) was freed from the adhering solvent in an air-oven. It was crystallised from rectified spirit as colourless needles, m. p. 185° . Successive crystallisations from benzene and ethyl acetate raised the m. p. to $188-89^{\circ}$. The product distilled at $150-160^{\circ}/0.1$ mm., m. p. $188-89^{\circ}$ even after recrystallisation from benzene, ethyl acetate and alcohol ; yield 0.65 g.

Isolation of a crystalline Compound of m. p. $157-58^{\circ}$.—The alcoholic mother-liquor from the residue (A) was concentrated and the second crop of crystals obtained was of crude bergapten. Finally the alcoholic mother-liquor was diluted with water and eventually dull yellow needles of m. p. $157-58^{\circ}$ were obtained from dilute alcohol. The product was distilled in *vacuo* ($140-150^{\circ}/0.1$ mm.). The m. p. did not rise on recrystallisation from ethyl acetate and benzene ; yield 0.33 g.

Treatment of the filtrate (B) : Isolation of Byakangelicin.—Petroleum ether (b. p. $40-60^{\circ}$) was added to the filtrate (B) to turbidity and the mixture was kept in a frigidaire overnight. A dark pasty solid separated and it was filtered, washed with benzene to remove adhering oil and crystallised twice from dilute alcohol as light yellow needles, m. p. $117-20^{\circ}$. The filtrate (C) containing benzene and petroleum ether was collected. The substance was further purified through successive crystallisations from benzene and ethyl acetate, m. p. $120-24^{\circ}$. Finally the product was subjected to vacuum sublimation and the yellow solid distilling at $200-210^{\circ}/0.1$ mm. had the melting point $120-24^{\circ}$, which was unchanged on crystallisation from benzene and ethyl acetate. The alcoholic mother-liquor when diluted with water deposited a second crop of impure byakangelicin. Benzene and ethyl acetate mother-liquors deposited on concentration a further quantity of the same substance. Total yield is 2.2 g.

Isolation of allo-Imperatorin.—The filtrate (C) was freed from the mixture of solvents by distillation and the residual oil was subjected to the method of Späth and Socias (*Ber.*, 1934, 67, 59).

The oil was cooled to about 15° and to it were added 200 c. c. of 20% methyl alcoholic potash with constant shaking. The mixture was allowed to stand for an hour at the same temperature and then poured into 1.5 litres of ice-water. The mixture was then extracted five times with ether to remove unsaponifiable matter. The alkaline aqueous portion was acidified with hydrochloric acid (Congo red) and allowed to stand overnight. A dark, thick oil mixed with crystalline solid separated.

The oily layer was separated, filtered in a pump, washed with ether and the residue (D) collected. The filtrate was freed from the solvent and the residual oil was kept overnight, whereby a pasty solid was obtained. The pasty solid was treated with a little alcohol and filtered, the filtrate being rejected. The residue was twice crystallised from alcohol and finally from glacial acetic acid as yellow shining plates, m. p. 229° , yield 0.88 g.

Purification of the residue (D) : Isolation of two compounds of m. p. 231° and $202-204^{\circ}$.—The residue (D) was crystallised three times from alcohol as pale yellow

shining plates, m. p. 200-204°. A second crop of crystals was obtained by diluting the alcoholic mother-liquors.

The crystalline compound of m. p. 200-204° was a mixture of two compounds, one being readily soluble in alkali carbonates and bicarbonates, caustic alkali and in ammonia. Consequently the substance was treated with a solution of sodium bicarbonate and kept overnight. The insoluble portion was filtered off, washed with water, and crystallised from ethyl acetate as light yellow needles, m. p. 231°. Further crystallisation from alcohol did not raise the melting point. The alkaline filtrate was acidified with hydrochloric acid, the colourless solid was filtered, washed with water and crystallised from alcohol as colourless shining plates, m. p. 202-204°. The melting point did not rise on crystallisation from glacial acetic acid, yield 3 g.

Identity of the Compound of m. p. 188-89° with Bergapten.—The substance is neutral to litmus and indifferent towards ferric chloride. It is insoluble in dilute aqueous alkali, but soluble in concentrated sulphuric acid with a deep yellow colour. An alcoholic solution of the substance turns yellow on addition of aqueous alkali and the alkaline solution remains clear on dilution. Original substance is recovered on acidification of the alkaline solution. The mixed m. p. with an authentic sample of bergapten is 188-89°. (Found in a sample dried over P_2O_5 in vacuum at 110-15°: C, 66.80; H, 3.98; OMe, 14.54; M. W. 218.6. Calc. for $C_{12}H_8O_4$: C, 66.66; H, 3.70, OMe; 14.35 per cent. M. W., 216).

Constitution of the Compound (m. p. 157-58°).—The compound is insoluble in dilute aqueous alkali and gives no coloration with ferric chloride, showing the probable absence of phenolic hydroxyl group. The substance dissolves in alcoholic potassium hydroxide from which the original substance may be recovered on acidification. (Found in a sample dried over P_2O_5 in vacuum at 100°-105°: C, 66.10; H, 3.80; OMe, 14.76. Calc. for $C_{12}H_8O_4$: C, 66.66; H, 3.70; OMe, 14.35 per cent).

Action of Alcoholic Potash on the Compound (m. p. 157-58°): Isomerisation to Bergapten.—The substance (0.1 g.) was refluxed with moderately concentrated alcoholic potash for 1 hour on a water-bath. The solution was then cooled, diluted with water and acidified. The solid thus obtained, crystallised from alcohol, m. p. 188-89° (mixed m. p. with an authentic specimen of bergapten, 188-89°).

Identity of the Compound (m. p. 120-24°) with Byakangelicin.—The substance is readily soluble in alcohol, benzene, chloroform and it crystallises from ethyl acetate in yellow shining flakes. It is neutral and gives no coloration with ferric chloride. It dissolves in cold concentrated sulphuric acid with a deep yellow colour. It is readily soluble in cold and boiling alcoholic potash from which the original compound is recovered on acidification. (Found in a sample dried over P_2O_5 in vacuum for 8 hours at 110°: C, 61.35; H, 5.85; OMe, 9.83. Calc. for $C_{17}H_{16}O_7$: C, 61.07; H, 5.38; OMe, 9.28 per cent).

Diacyl Byakangelicin.—The substance (0.1 g.) was gently refluxed with acetic anhydride (5 c. c.) and dry pyridine (2 drops) for 2 hours. The mixture was cooled, diluted with water, heated on a steam-bath for 10 minutes. The solid separating was crystallised from dilute alcohol as colourless silky needles, m. p. 112°. (Found in a

sample dried over P_2O_5 in vacuum for 2 hours at $85-90^\circ$: C, 60.03 ; H, 5.44. Calc. for $C_{21}H_{22}O_6$: C, 60.28 ; H, 5.26 per cent).

Action of glacial acetic acid and sulphuric acid on Byakangelicin : Isolation of a Phenol (m. p. 219°).—The substance (0.50 g.) was dissolved in a mixture of glacial acetic acid (12 c. c.) and concentrated sulphuric acid (12 drops) and the solution was just heated to boiling under reflux for 30 minutes. The mixture was cooled and diluted with water. The yellow solid was filtered, washed with water and crystallised from dilute alcohol as yellow silky needles, m. p. 219° . This substance is readily soluble in dilute aqueous alkali but does not respond to ferric reaction. (Found in a sample dried over P_2O_5 in vacuum at $110-15^\circ$: C, 61.98; H, 3.64; OMe, 13.70. Calc. for $C_{12}H_8O_6$: C, 62.07 ; H, 3.45; OMe, 13.36 per cent).

Action of Methyl Iodide on the above Phenol: Formation of isoPimpinellin.—A solution of the phenol (0.10 g.) in dry acetone was refluxed with methyl iodide (5 c. c.) and anhydrous potassium carbonate (2 g.) for 2 hours on a water-bath. The solution was then cooled, filtered, freed from the solvent and the residue crystallised from alcohol as yellow shining needles, m. p. 149° . The methyl ether is insoluble in cold alkali. The mixed m. p. with the authentic specimen of isopimpinellin is also 149° . (Found in a sample dried over P_2O_5 in vacuum at 100° for 2 hours : OMe, 25.14. Calc. for $C_{13}H_{10}O_5$: OMe, 25.20 per cent).

Identity of the Compound (m. p. 229°) *with allo-Imperatorin*.—It was obtained as yellow shining plates, readily soluble in ethyl acetate, benzene but sparingly soluble in alcohol and glacial acetic acid. It is neutral to litmus, and does not give any coloration with ferric chloride. It is soluble in cold and boiling aqueous alkali from which the original substance is recovered on acidification. It is insoluble in alkali carbonate and bicarbonate but soluble in cold concentrated sulphuric acid with a deep yellow colour. It melts at 229° when mixed with an authentic specimen of allo-imperatorin. (Found in a sample dried over P_2O_5 in vacuum at 110° : C, 70.68; H, 5.15. Calc. for $C_{18}H_{14}O_4$: C, 71.11 ; H, 5.18 per cent).

Acetylation of allo-Imperatorin.—The acetyl derivative was prepared with acetic anhydride and pyridine in the usual manner. The solid crystallised from dilute alcohol as colourless shining flakes, m. p. 137° . It melts at 136° when mixed with an authentic sample of the acetyl derivative of allo-imperatorin.

Methylation of allo-Imperatorin.—The methyl ether was prepared with methyl iodide in the usual manner. The product crystallised from dilute alcohol as pale yellow silky needles, m. p. 113° . It is insoluble in dilute aqueous alkali. It also melts at 113° when mixed with an authentic sample of the methyl ether of allo-imperatorin. (Found in a sample dried over P_2O_5 in vacuum at 90° : C, 71.60 ; H, 5.46 ; OMe, 10.80. $C_{17}H_{14}O_4$ requires C, 71.83 ; H, 5.63 ; OMe, 10.91 per cent).

The author's best thanks are due to Dr. D. Chakravarti, D. Sc., for giving facilities to work in his laboratory and valuable advice and keen interest during the progress of this work and also to Mr. N. Ghosh, M. Sc., for microanalyses of some of the compounds.

CONDENSATION OF ALDEHYDES WITH AMIDES. PART XV. OF 6-BROMOPIPERONAL

BY KANTILAL C. PANDYA AND RAM LABHAYA SETHI

6-Bromopiperonal has been condensed with amides; the condensation went fairly well with acetamide, propionamide and *n*-heptamide, giving 6-bromopiperonal-bisamides. It gave about 67% yield of the corresponding biuret with urea. The yield from the condensation with benzamide was poor, and that from formamide was nil. Different conditions have been specified.

6-Bromopiperonal has been condensed with several amides. On the whole the yields were much less than those obtained from the condensations with amides of piperonal and of 6-nitropiperonal (Pandya and Varghese, *Proc. Ind. Acad. Sci.*, 1941, **14A**, 18, 25). This is almost a contrast with the 6-bromopiperonal-malonic acid condensation, where the yield was excellent (Pandya, Miss Pandya and Sethi, *Proc. Ind. Acad. Sci.*, 1948, in the press). The products were all of the bisamide type. The main difficulty was the very easy volatility of 6-bromopiperonal, so that reactions in the dry state without a solvent did not proceed, the aldehyde soon subliming away to the top of the flask. Different solvents or condensing agents were found useful, such as pyridine, acetic acid or pyridine acetate, the highest yield coming from one or the other in the case of different amides. Pyridine was ineffective except in the cases of *n*-heptamide and of urea, which in the presence of pyridine gave the highest yields of 36% and 67% respectively. The yields from acetamide and propionamide were the next best, being 29% and 23% respectively. Benzamide gave a very poor yield of about 4% and formamide did not seem to condense at all, neither did piperonal or 6-nitropiperonal condense with formamide.

Temperature was a very important factor. No condensation took place on the water-bath; the optimum temperature was found to be 105°-110°, and the time of the heating varied from 8 hours to nearly 15 hours.

All the products obtained are white, needle-shaped crystals, melting above or very slightly below 200°. They are insoluble in water or in the usual organic solvents, except alcohol, which could be used for recrystallisation. They do not react with Baeyer's reagent or bromine water in the cold.

EXPERIMENTAL

Condensation with Benzamide.—The easy sublimability of the 6-bromopiperonal was the main difficulty for which no condensation product could be obtained in some of the earlier experiments. Heating alone on a water-bath (2 hours), heating at 105-110° (2 hours), heating with pyridine (1:2:1.5 mol.) at 105-110° for 14 hours, heating at 120-130° for 3 hours with pyridine, and with absolute alcohol (water-bath) for 14 hours, at 105-110° for 15 hours with pyridine (3 mols. and 6 mols.), all these failed to give any product, the reactants being recovered unchanged for the most part.

Heating with pyridine acetate (aldehyde 1.2 g., amide 1.2 g., pyridine 3 drops and glacial acetic acid 1 c. c., 1:2:0.1:3.5 mol. nearly) at 105-110° for 14 hours gave a small

amount of a product, which, treated in the usual way, melted (crude) at 210° (higher than the melting points of the aldehyde or of the amide).

Another experiment with the same amounts of the aldehyde and the amide and 2 c. c. of glacial acetic acid (1:2:7 mol.) and heating at $105-110^{\circ}$ for 15 hours gave 0.1 g. of a product, melting at 227° . It came out in fine, silky white needles (hot alcohol). A second experiment was repeated with double the quantities of each and gave 0.2 g. of the same, the yield being 4.4% of theory (as *bisbenzamide*). It was almost insoluble in ether, benzene and chloroform. It did not affect in the cold Baeyer's reagent, bromine water or bromine in chloroform solution. It gave a yellow colour with cold concentrated sulphuric acid; but when water was added, a light violet coloured ring developed at the junction of the two layers which turned brown on shaking. (Found: Br 17.24. 6-Bromopiperonyl-*bisbenzamide*, $C_{22}H_{17}O_4N_2$ Br, requires Br, 17.66 per cent).

Condensation with Acetamide.—When the aldehyde and acetamide were heated alone (1:4 mol.) on a water-bath or at $105-110^{\circ}$, in two hours the aldehyde had all sublimed. Some product was obtained with pyridine acetate (aldehyde 1.2 g., acetamide 1.2 g., pyridine 0.2 g. and glacial acetic acid 0.5 c. c., i. e. 1:4:0.5:1.75 mol.) at $105-110^{\circ}$ and on 12 hours' heating. The crude product (0.6 g.) was obtained in the usual way, melting at 225° and at 230° after purification. The yield was 0.4 g. (23% of theory of the *bis*-acetamide). A second experiment, with double the quantities, gave 1 g. yield (29% of theory). With pyridine alone (1:4:1 mol.) the yield was very small.

Its properties were similar to those described for the *bisbenzamide*. Cold concentrated sulphuric acid gave a light yellow colour; addition of water produced a violet ring, and shaking gave a pinkish brown colour. (Found: Br, 23.84. 6-Bromopiperonyl-*bis*acetamide, $C_{12}H_{13}O_4N_2$ Br, requires Br, 24.31 per cent).

Condensation with Propionamide.—There was no condensation when the aldehyde and propionamide (1:2) were heated alone on a water-bath or at $105-110^{\circ}$. With glacial acetic acid (1:2:1.75 mol.) and on heating at $105-110^{\circ}$ for 9 hours about 0.6 g. of a product melting at 213° was obtained. Recrystallisations (hot alcohol, twice) raised the melting point to 225° which did not rise further. The yield was 0.4 g. (23% of theory). In the presence of pyridine alone (1:2:1 mol.) and heating at $105-110^{\circ}$ for 9 hours gave only about 3% yield. Heating for 16 hours with glacial acetic acid (1:1:3.5 mol.) gave again a 23% yield. Heating at $110-115^{\circ}$ raised the yield to 32%. White, needle-shaped crystals (hot alcohol) melting at 225° had the same properties as have been described for the *bisbenzamide*. (Found: Br, 21.93. 6-Bromopiperonyl-*bis*propionamide, $C_{14}H_{17}O_4N_2$ Br, requires Br, 22.41 per cent).

Condensation with n-Heptamide.—Heating the two alone was again found to be useless. Heating with glacial acetic acid (1:2:3.5 mol.) on a water-bath for 13 hours also gave negative result. The flask was then heated at $105-110^{\circ}$ for another 15 hours. The crude product was washed with chloroform (which dissolved both the amide and the aldehyde), then several times with warm water and then with ether; this gave a crude product melting at 181° and at 183° after recrystallisation; yield 0.8 g. (36% of theory). The same substance in the same yield was obtained when the condensation was carried out in the presence of pyridine (1:2:1 mol.) on a water-bath for 3 hours, and then at $105-110^{\circ}$ for 15 hours. Larger amounts of glacial acetic acid (1:2:7 mols.) did not augment the

yield (which was only 22%). The properties of the *bis-n*-heptamide were similar to those described above. (Found: Br, 16.69. 6-Bromopiperonyl-*bis-n*-heptamide, $C_{22}H_{23}O_4N_2Br$, requires Br, 17.06 per cent).

Condensation with Urea.—As usual, heating the two alone (aldehyde, 1.2 g. and urea, 0.6 g., 1:2 mol.) on a water-bath for 3 hours, made all the aldehyde sublime away without any condensation having taken place. Heating at 105–110° for 8 hours, however, had the desired effect. The mass melted and resolidified. By extracting with water and chloroform and filtering, a brownish product was obtained, which after purification melted at 198–99°, yield 1.15 g. It had the usual properties, given above, of the *bis*amides. (Found: Br, 25.02. 6-Bromopiperonyl-biuret, $C_{10}H_8O_4N_3Br$, requires Br, 25.48 per cent; 6-bromopiperonyldiurea, $C_{10}H_{11}O_4N_4Br$, requires Br, 23.46 per cent).

TABLE I
Maximum yields

Amide.	Piperonal.	6-Nitropiperonal.	6-Bromopiperonal.
Formamide	Nil	Nil	Nil
Acetamide	42%	61%	29%
Propionamide	36	15	23
<i>n</i> -Heptamide	77	55	36
Benzamide	64	25	4
Cinnammamide	82	82	Not tried
Urea	Not tried	Not tried	67

CHEMISTRY LABORATORY,
ST. JOHN'S COLLEGE, AGRA.

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CONDENSATION OF MALONIC ACID WITH ALDEHYDES. PART XXIII WITH *o*-ETHOXYBENZALDEHYDE

BY RAMESH CHANDRA GUPTA AND KANTILAL C. PANDYA

o-Ethoxybenzaldehyde has been condensed with malonic acid. In the presence of a trace of pyridine, it gave nearly a quantitative yield of *o*-ethoxycinnamic acid, m. p. 133-34°, in the absence of any condensing agent, it gave a small amount (8%) of the same acid with 68% of the *o*-ethoxybenzylidene-malonic acid.

o-Ethoxybenzaldehyde has been condensed by Perkin (*J. Chem. Soc.*, 1881, 39, 413) with sodium acetate and acetic anhydride in a sealed tube at 160-180°, as a result of which he obtained what he called β -ethyl-*o*-oxyphenylacrylic acid (m. p. 135°). The yield is not given, but it could not possibly be as good as is obtained in the present experiment. Here the *o*-ethoxybenzaldehyde, malonic acid and pyridine (in 1:1:0.16 mol.) were heated on a water-bath: one experiment in which the heating was done for 6 hours gave almost a quantitative yield of the same *o*-ethoxycinnamic acid. As is usual in these condensations, in the presence of pyridine, salicylaldehyde is the only aldehyde to give coumarin (Kurien and Pandya, *J. Indian Chem. Soc.*, 1934, 11, 824; Khan, Kurien and Pandya, *Proc. Ind. Acad. Sci.*, 1935, 1, 440) i. e. the *cis*-form; in all the others, as in *o*-methoxybenzaldehyde (Pandya and Vahidy, *ibid.*, 1937, 5A, 437) and in *o*-ethoxybenzaldehyde, the *trans*-form is the only form obtained.

An attempt was also made to obtain the undecarboxylated *o*-ethoxybenzylidene-malonic acid. This was obtained (m. p. 174-75°) when the aldehyde and malonic acid were heated alone on a water-bath for 4 hours, when about 8% yield of the *o*-ethoxycinnamic acid and 68% yield of the dibasic acid were obtained.

Stuart's method (*J. Chem. Soc.*, 1888, 53, 142) of heating the two with glacial acetic acid was also tried; the condensation did not appear to have taken place at all on the water-bath, even on 20 hours' heating. The temperature was gradually raised to 140°-150°, when a product came out, but at that temperature and with a long heating time it was only the monobasic *o*-ethoxycinnamic acid in about 60% yield. Comparison of the yields from salicylaldehyde and its methyl and ethyl ethers shows very clearly that while the hydroxy group in the *ortho* position has given the lowest yield, the methoxy and the ethoxy groups in the same position have given almost the theoretical yields in the presence of a trace of pyridine; when no condensing agent is used, the ethoxy derivative gives the best yield.

EXPERIMENTAL

In the presence of a trace of Pyridine.—*o*-Ethoxybenzaldehyde (1.5 g.), malonic acid (1.0 g.) and pyridine (0.13 g.) (prepared as usual, and in 1:1:0.16 mol. proportion) were heated together on a water-bath for 4 hours. The reaction was very quick, as liquefaction and formation of a white solid took place in 1 hour. After cooling over-

night, the product was dissolved in sodium bicarbonate solution, and it gave on acidification a white substance. It was washed well with water, and on drying it melted at 130° ; yield 1.3 g. on recrystallisation (alcohol), the final melting-point was $133-34^{\circ}$. Perkin gives m. p. 135° (*loc. cit.*). Titration against caustic soda solution gave equivalent, 191.5; *o*-ethoxycinnamic acid, $C_{11}H_{12}O_3$, requires equiv., 192. The yield was 67.7%.

In a second experiment the heating was for 6 hours, when the yield was 1.9 g. (99%):

In the absence of any Condensing Agent.—The acid and the aldehyde were heated alone (1:1 mol.) on a water-bath for 4 hours. A yellow product was obtained, which was treated with sodium bicarbonate solution and dilute hydrochloric acid; a white precipitate was then obtained and from the filtrate, a yellow substance was obtained by extraction with ether.

The white substance, crystallised from alcohol, melted at $133-34^{\circ}$, and a mixed melting point with the product of the previous experiment showed that it was the *o*-ethoxycinnamic acid (titration with NaOH solution gave equiv., 191.6). The yield was only 0.16 g. (8.3% of theory).

The crude yellow product melted at 167° , and after recrystallisation (alcohol) yellow needles were obtained, m. p. $174-75^{\circ}$ (with effervescence). When heated at 175° for 15 minutes till the effervescence had stopped, and then cooled, it changed into a solid melting at $127-28^{\circ}$, which is near to that of the mono-acid.

The yellow acid is the corresponding malonic acid. [Found: equivalent (by titration), 120.0; (by silver salt), 120.1; M. W. (Rast), 233.5. *o*-Ethoxybenzalmalonic acid, $C_{12}H_{14}O_5$, requires equiv., 118.0; M. W., 236]. The yield was 1.6 g. (68% of theory). The total yield of the two acids was thus over 76%.

TABLE I

Aldehyde	Heated at for	Catalyst.	Product.	Yield	Ref.
Salicylaldehyde	100°. 18 hrs.	Pyrrolidone trace	Coumarin- carboxylic acid	57%	Kurien & Pandya, (<i>J. I. C. S.</i> , 1944, 11, 823)
<i>o</i> -Ethoxy- benzaldehyde	" 5	"	<i>o</i> -Methoxy- cinnamic acid	Nearly 100%	Pandya & Vahidy, <i>Proc.</i> <i>Ind. Acad. Sci.</i> , 1937, 8, 439)
<i>o</i> -Ethoxy- benzaldehyde	" 6	"	<i>o</i> -Ethoxy- cinnamic acid	"	(Present paper)
Salicylaldehyde	" 5	None	<i>o</i> -Coumarin- carboxylic acid	11%	Khan, Kurien, Pandya, <i>Proc.</i> <i>Ind. Acad. Sci.</i> , 1935, 1, 441)
<i>o</i> -Methoxy- benzaldehyde	" "	"	<i>o</i> -Methoxy- cinnamic acid	48%	Pandya & Vahidy (<i>loc. cit.</i>)
<i>o</i> -Ethoxy- benzaldehyde	" 5	"	Mixture <i>o</i> -ethoxy- cinnamic acid & <i>o</i> - ethoxy benzylidene- malonic acid	8% 68%	Present Paper

In the presence of Glacial Acetic Acid.—The same quantities of the aldehyde and the acid were heated with 6 g. of glacial acetic acid (1:1: 3.6 mol.) on a water-bath for 20 hours ; no condensation could be detected to have taken place in a test sample taken out. The temperature was then raised to 110° and maintained for 7 hours, yet no product could be detected. Four hours' heating at 125-130° also proved ineffective. Only when the oil-bath was raised to 140-150° and maintained for 4 hours, a solid began to separate out. The whole mixture was then poured into a large quantity of water, the insoluble portion dissolved in sodium bicarbonate solution, and reprecipitated by means of dilute acid ; after filtering, washing and drying it was found to melt at 131° ; on recrystallisation the melting point rose to 133-34° and it was identified as the *o*-ethoxycinnamic acid. The yield was 1.1 g. (about 60%). No dibasic acid was isolated : it must have been first formed, but was not isolable.

CHEMISTRY LABORATORY,
ST. JOHN'S COLLEGE, AGRA.

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A NOTE ON THE SAPONIN FROM *SAPINDUS LAURIFOLIUS*, VAHL

By H. G. BISWAS

Two species of soapnut tree, namely *Sapindus mukorossi*, Gaerten and *Sapindus laurifolius*, Vahl, are indigenous to India. Saponin ($C_{17}H_{26}O_{10}$) has been isolated by Weil (*Arch. Pharm.*, 1901, 289, 363) from *S. mukorossi*. The sapogenin occurring in *S. mukorossi* and in *Sapindus saponaria*, Linn. has been proved to be identical with hederagenin (Jacobs, *J. Biol. Chem.*, 1925, 63, 621; 64, 379). The preparation of crude saponin (in an yield of 17.21%) from soapnuts derived from *S. mukorossi* has been described by Sarin and Beri (*Ind. Eng. Chem.*, 1939, 31, 712).

In the present paper, a method for the isoation of pure saponin from *S. laurifolius* has been described. The method differs in some respects from the one followed by Sarin and Beri (*loc. cit.*).

The pure saponin melted at 145° and on hydrolysis it furnished a sapogenin, m. p. $328-29^{\circ}$. Acetate of the sapogenin was found to melt at 170° . The sapogenin is believed to be identical with hederagenin (m. p. $327-29^{\circ}$; diacetate, m. p. $170-75^{\circ}$, recorded by Jacobs, *loc. cit.*).

Isolation of Saponin.—The pericarp which constituted 46% of the soapnut (*S. laurifolius*) was dried in steam in vacuum and powdered. The powder (100 g.) was exhausted with ethyl acetate (500 c.c.) in a soxhlet. The solvent in the extract was then distilled off and the residue dissolved in water, boiled with animal charcoal and filtered. The filtrate was evaporated to dryness in a steam-bath. The powdered residue was dissolved in the minimum quantity of absolute alcohol and the solution poured into dry ether with stirring. The flocculent precipitate was removed, redissolved in boiling distilled water, charcoaled and filtered. The filtrate was concentrated in a steam-bath and finally dried in a steam-bath under reduced pressure. A white substance, m. p. 145° , was thus obtained (14.5 g.). The saponin is insoluble in ether, chloroform, benzene and petroleum ether but is soluble in methyl and ethyl alcohol, water and warm pyridine. It is acidic and dissolves in concentrated sulphuric acid. The orange sulphuric acid solution turns violet after some time. (Found: C, 56.20; H, 7.74 per cent).

Hydrolysis of the Saponin: Isolation of Hederagenin.—The saponin was hydrolysed with dilute methyl alcohol (1:1) containing 5% hydrochloric acid in the usual way. The resulting sticky mass was separated and washed with petroleum ether which removed an oil having terpene-like odour. The insoluble solid substance on crystallisation from methyl alcohol formed rhombic crystals melting at $328-29^{\circ}$ (after sintering at $323-24^{\circ}$). The sapogenin is insoluble in ether, water, benzene and petroleum ether. It is sparingly soluble in cold alcohol but readily soluble in pyridine and dilute alkali. It dissolves in concentrated sulphuric acid to a colourless solution which becomes deep red after sometime. [Found: C, 76.39; H, 10.10. $C_{31}H_{50}O_4$ (hederagenin) requires C, 76.48; H, 10.36 per cent].

The *diacetate*, prepared in the usual way, formed colourless needles, m. p. 170° . [Found: C, 73.51; H, 9.19. $C_{35}H_{54}O_8$ (hederagenin diacetate) requires C, 73.63; H 9.54 per cent].

The author's best thanks are due to Mr. N. N. Ghosh of the University College of Science, Calcutta, for carrying out microanalyses of the compounds.

SIR PRAFULLA CHANDRA RESEARCH LABORATORY,
BENGAL CHEMICAL AND PHARMACEUTICAL WORKS, LTD.
CALCUTTA.

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REVIEW

Modern Chemistry, Some Sketches of its Historical Development: By A. J. Berry, M.A. Published by Cambridge University Press, 1946. Royal 8vo, pp.240+x. Price 10 sh. 6d net.

The book, besides having an elaborate table of contents, and both a subject and an author index, is composed of nine chapters on classical atomic theory, electrochemistry, stereochemistry, radioactivity, elements isotopes and atomic numbers, some experimental studies on gases, some problems of solutions, some essential features of chemical change and a retrospect. No detailed history of any topic is attempted. In fact, the book is claimed to be no substitute for any of the excellent classical works on historical chemistry. It is, however, realized that the proper attitude of the student to a subject should be based upon a knowledge of the order in which men in different times have tackled its problems and contributed to its present state of development; and indeed, judged from this standpoint, the attempt has been entirely satisfactory. The chapters, evenly spread over the volume, are "nearly self-contained and largely independent of the others", and in their selection and arrangement, the author has been largely guided by his teaching experience. The style is lucid, and the treatment of historical material able and concise, in spite of its great variety. Some French and German passages have been quoted in Chapters I, III, VIII etc., whose English renderings in parentheses would be desirable. Nuclear equations in pp. 113 and 114, especially one in the former, are not sufficiently explanatory, and should be replaced by more conventional ones such as used in p. 129. The rayless disintegration of mesothorium 1 to mesothorium 2, mentioned by the author (p.102), also needs further elucidation.

The book is well printed and remarkably free from errors and irregularities.

J. G.

ERRATA

In the Review, published in the February issue of this journal, the last line in p. 101 should be read as "not large, but..." for "large, but..."

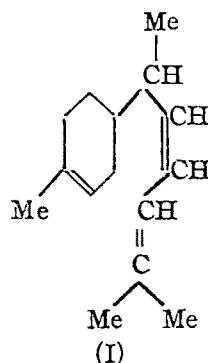
In p. 100, and line, "Emphraim" should be read as "Ephraim."

STUDIES IN SESQUITERPENES. PART II. SYNTHESIS OF ZINGIBERENE

BY SAILENDRA MOHAN MUKHERJEE

A synthesis of the monocyclic sesquiterpene, zingiberene has been achieved.

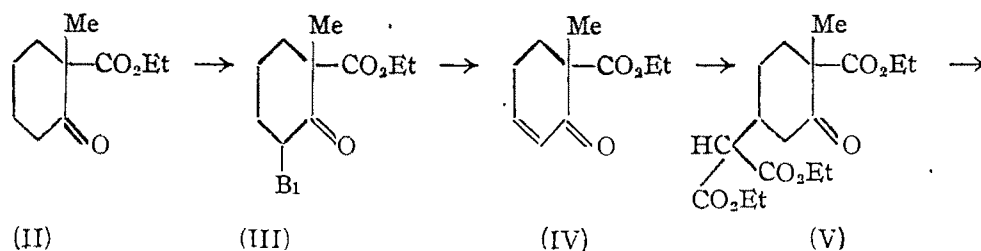
The present investigation was initiated with a view to synthesising the monocyclic sesquiterpene, zingiberene, for which the following constitution was suggested by Ruzicka and Van Veen (*Annalen*, 1929, **468**, 143), on the basis of analytical evidences. In the following lines are described the experiments ending in the complete synthesis of the sesquiterpene.

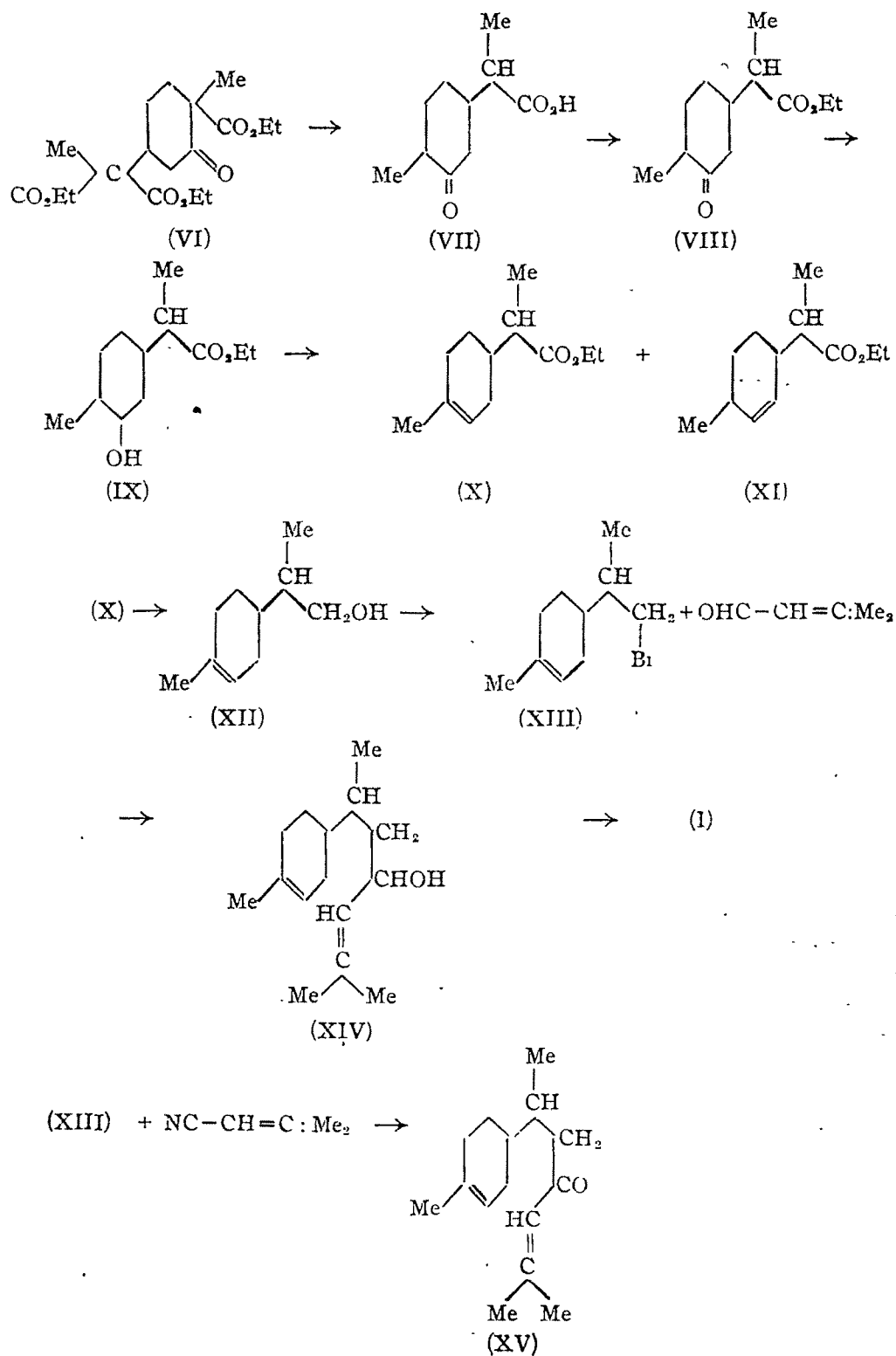


The important features of the above structure are the presence of the *sec*.-isooctyl chain which is the side-chain of the sterols (cholesterol, etc.) and the three double bonds two of which are in conjugation.

Kuhn and Grundmann (*Ber.*, 1938, **71**, 442) have synthesised a series of polyenes (having a large number of conjugated double bonds) taking advantage of the reaction between the suitable Grignard reagent and the proper $\alpha\beta$ unsaturated ketones or aldehydes followed by dehydration of the resulting carbinol which splits off the elements of water very readily owing to the double bond, already present, facilitating the formation of the conjugated system. The above authors (*loc. cit.*) obtained from sorbaldehyde and ethyl magnesium bromide 1 : 6-dimethylhexatriene, previously prepared by other methods (Urion, *Ann. chim.*, 1934, *xi*, 1, 5).

Zingiberene has been successfully synthesised following the reactions similar to those adopted by Kuhn *et al.* (*loc. cit.*) for the synthesis of conjugated systems, starting from ethyl 2-methylcyclohexanone-2-carboxylate as follows:—





Ethyl 2-methylcyclohexanone-2-carboxylate (II) was brominated according to the conditions laid down by Conrad and Kriechgauer (*ibid.*, 1897, **30**, 856). The bromo-ester (III), thus obtained, could not be purified by distillation in *vacuo* as it underwent profuse decomposition due presumably to the easy formation of a keto-lactone (cf. Conrad and Kriechgauer, *loc. cit.*). It was, however, found convenient to proceed for the next treatment with the crude bromo-ester (III) after removal of hydrobromic acid in *vacuo*.

Considerable difficulty was experienced in the successful treatment of the bromo-ester (III) with quinoline. A temperature higher than 160° has been found to decrease the yield considerably; the duration of heating of the reaction mixture has also influence on the yield. The optimum conditions, as found by trials, consist in heating the reaction mixture at 150°-160° (the temperature must be below 160°) for $\frac{1}{2}$ hour, followed by working up of the reaction mixture as quickly as possible. It may be mentioned that diethylaniline could be used in place of quinoline, but the yield of the desired product (IV) is much diminished in that case.

Michael reaction was first applied to $\alpha\beta$ -unsaturated ketones by Vorländer (*Annalen*, 1902, **66**, 320) and later by various workers. Bartlett and Woods (*J. Amer. Chem. Soc.*, 1940, **67**, 2937) obtained cyclohexanone-2-acetic acid by condensing Δ^2 -cyclohexenone with ethyl malonate in presence of a trace of sodium ethoxide.

Now, ethyl 2-methyl- Δ^2 -cyclohexenone-2-carboxylate (IV) was allowed to react with ethyl malonate in presence of a small amount of sodium ethoxide following exactly the conditions worked out by Bartlett and Woods (*loc. cit.*), when the normal addition product (V) was obtained in fairly good yield. It was interesting to note that no fission of the molecule was observed (cf. Simonsen *et al.*, *J. Chem. Soc.*, 1935, 313; Robinson *et al.*, *ibid.*, 1937, 61) in presence of sodium ethoxide. When the reaction was carried out in presence of one molecular equivalent of sodium ethoxide, normal addition took place, though in poor yield, the product giving no coloration with alcoholic ferric chloride solution (Holden and Lapworth, *ibid.*, 1931, 2370).

Considerable difficulties were encountered in successfully methylating the Michael condensation product. Condensation of the unsaturated keto-ester (IV) with ethyl methylmalonate in presence of traces of sodium ethoxide was attempted but with poor yield. It was then observed that although the possible retrogression (Michael, *Ber.*, 1900, **33**, 3731; Ingold, *J. Chem. Soc.*, 1921, **119**, 1976; Michael and Ross, *J. Amer. Chem. Soc.*, 1933, **55**, 1632) took place with "molecularised" sodium in benzene, the methylation of the Michael product by its treatment with sodium ethoxide in molecular proportion in large excess of alcohol and at a very low temperature (cf. Cope *et al.*, *J. Amer. Chem. Soc.*, 1938, **60**, 2903), followed by a quick refluxing after the addition of methyl iodide proceeded smoothly with negligible retrogression.

The methylated product underwent smooth hydrolysis when refluxed with excess of concentrated hydrochloric acid for a long time. The keto-acid (VII), thus obtained, was esterified by alcohol-sulphuric acid method and the reduction of the resulting keto-ester (VIII) according to the conditions laid down by Young, Hartung and Crossley (*ibid.*, 1936, **58**, 100) presented no difficulty and the corresponding hydroxy-ester (IX) was obtained in almost quantitative yield. Analysis of the above hydroxy-ester (IX)

showed that the exchange of the ethyl group of the ester with isopropyl group did not take place to any appreciable extent (Robinson *et al.*, *loc. cit.*). Dehydration of the hydroxy-ester (IX) was effected with P_2O_5 in benzene when ethyl α -(4-methyl- Δ^2 -cyclohexenyl)-propionate (X) was obtained, contaminated with small amounts of ethyl α -(4-methyl- Δ^2 -cyclohexenyl)-propionate (XI) which was separated through repeated fractionations (cf. Price and Karabinos, *J. Amer. Chem. Soc.*, 1940, **62**, 1159). It may be pointed out that during a series of preliminary experiments it was observed that 2-methylcyclohexanol, obtained by reduction with aluminium isopropoxide in dry isopropyl alcohol, gave on dehydration with P_2O_5 in benzene a mixture of 1-methyl- Δ^1 -cyclohexene and 1-methyl- Δ^2 -cyclohexene. In order to determine the direction in which dehydration preponderated, the above cyclohexene mixture was oxidised with potassium permanganate (cf. Price, *ibid.*, 1939, **61**, 1848). Almost 80% of the oxidation product were found to consist of δ -acetylvaleric acid, identified through its semicarbazone. This shows that unsaturation takes place mainly towards the methyl group.

The Δ^2 -isomer (X) was then subjected to Bouveault's reduction with sodium and alcohol. Reduction of similar cyclohexenyl systems was accomplished by Cook and Dansi (*J. Chem. Soc.*, 1935, 500) and Cook and Lawrence (*ibid.*, 1937, 817). The yield in the Bouveault's method has been much improved by using absolute alcohol, dried over metallic calcium (cf. Rydon, *ibid.*, 1936, 594).

The alcohol (XII), thus obtained, was converted into the corresponding bromide (XIII) by treatment with phosphorus bromide and pyridine according to Linstead *et al.* (*ibid.*, 1937, 1971).

For the preparation of β -methylcrotonitrile, advantage was taken of the reaction between ketones and cyanoacetic acid in presence of an excess of piperidine when condensation took place with simultaneous elimination of carbon dioxide (Schemjakin and Trachtenburg, *Compt. rend. U. S. S. R.*, 1939, **24**, 763) with an excellent yield of β -methylcrotonitrile. The same nitrile was also obtained, though in much inferior yield, by dehydrating the amide of $\beta\beta$ -dimethylacrylic acid with P_2O_5 ; the latter was prepared by oxidation of mesityl oxide with potassium hypobromite (Kohn, *Monatsh.*, 1903, **24**, 771; Vogel, *J. Chem. Soc.*, 1937, 1606).

The Grignard complex, prepared from (XIII), was allowed to react with β -methylcrotonitrile in thiophen-free benzene solution according to Butenandt *et al.* (*Ber.*, 1938, **71**, 1486). The product, obtained by decomposing the ketimine with warm glacial acetic acid, consisted of a mixture of the ketone (XV) and, as an undesirable impurity, the hydrocarbon produced by Wurtz-condensation between one molecule of the Grignard reagent and a molecule of the bromide (XIII). This hydrocarbon was separated by repeated fractionations. It was observed that whenever the ketone (XV) was distilled, some amount of a high boiling product remained in the distilling flask, possibly owing to the great tendency of the $\alpha\beta$ -unsaturated ketone to polymerize. Although this ketone (XV) is not known to occur in nature, it may be termed "Zingiberone" in view of the structural similarity with zingiberene.

The extremely poor yield of the ketone (XV) led the author's attention to the reaction between the Grignard reagent from the bromide (XIII) and β -methylcrotonaldehyde, which was expected to afford directly the alcohol (XIV).

β -Methylcrotonaldehyde was first prepared by Fischer (*Ber.*, 1935, **68**, 1726). It has now been prepared in this laboratory in satisfactorily good yield by taking advantage of the excellent modification of Reissert's method (Reissert, *ibid.*, 1905, **38**, 1610) by Grosheintz and Fischer (*J. Amer. Chem. Soc.*, 1941, **63**, 2021). Owing to the easy tendency of β -methylcrotonaldehyde to undergo autoxidation and polymerization, all the operations in the method of its preparation were accomplished in an atmosphere of nitrogen and the distilled aldehyde, kept in an atmosphere of nitrogen, was employed immediately in the next operation. The Grignard complex prepared from (XIII) was reacted with β -methylcrotonaldehyde in ether resulting in the alcohol (XIV) in fairly good yield, which without further purification, was subjected to treatment with *p*-toluene-sulphonic acid according to the method of Kuhn and Grundmann (*loc. cit.*). After repeated fractionations, a few drops of the desired hydrocarbon (I) were obtained.

Refractive index n_D^{20} , 1.4954; sulphur dehydrogenation of the synthetic material at 180-200° gave cadalene (b. p. 161-163°/15 mm.) which has been identified by preparing its picrate (m. p. 115-16°). The melting point did not show any depression after mixing with the picrate of an authentic sample of cadalene.

EXPERIMENTAL

Ethyl 2-Methyl- Δ^5 -cyclohexenone-2-carboxylate (IV).—2-Methyl cyclohexanone-2-carboxylate (37 g.) was allowed to react with 11 c. c. of bromine, added dropwise with ice-cooling and continuous shaking. The bromine was absorbed as soon as it fell on the liquid. In the later part of the addition, copious evolution of hydrogen bromide took place. After the addition, the mixture was allowed to stand in the cold for half an hour; hydrogen bromide was driven off with the water-pump, and then the flask was evacuated at 5 mm. for 1 hour. To this bromo derivative was added freshly distilled quinoline (40 g., 1.5 mol.) and the solution was heated in an oil-bath at 150°-160° for half an hour when the reaction mixture assumed a deep red colour; it was then cooled rapidly under water. The whole was then poured into iced sulphuric acid. The dilute solution was then extracted with ether, the ethereal layer washed with dilute sulphuric acid, sodium bicarbonate solution and water, and dried. On distillation in *vacuo* the residue, left after evaporation of the solvent, gave 26 g. of the unsaturated keto-ester, b.p. 112-14°/10 mm. (Found: C, 65.76; H, 7.35. $C_{10}H_{14}O_3$ requires C, 65.93; H, 7.7 per cent).

In a separate experiment unsaturation was effected with diethylaniline (freshly distilled). The quantity of diethylaniline used was two molecular proportions; otherwise, the procedure was exactly the same as described above, but as the yield in this case was very poor quinoline was preferred.

Ethyl 2-Methyl-5-(diethylmalonate)-cyclohexanone-2-carboxylate (V).—Sodium (0.1 g.) was dissolved in absolute alcohol (50 c.c.) and ethyl malonate (35 g.) was added to it. The solution was chilled to below -5° and the above unsaturated ester (IV, 36.4 g.) in 15 c.c. of anhydrous alcohol was added dropwise with shaking. The flask was then allowed to stand in the ice-salt mixture for 2 hours and allowed to warm up to room temperature and kept overnight. The product was worked up by destroying the sodium ethoxide with a little acetic acid and after dilution with brine the

solution was extracted with ether. The ethereal extract was washed twice with water and dried. After removing the ether, the residue was distilled in vacuum when a thick liquid came over at $192^{\circ}/5$ mm., yield 42.5 g. (Found : C, 59.82; H, 7.3. $C_{17}H_{26}O_7$ requires C, 59.64; H, 7.6 per cent).

The *semicarbazone*, prepared in the usual way, crystallised from aqueous alcohol, m.p. 126° . (Found : N, 10.6. $C_{18}H_{26}O_7N_3$ requires N, 10.52 per cent).

Condensation of Ethyl 2-Methyl- Δ^5 -cyclohexenone-2-carboxylate (IV) with Ethyl Malonate in presence of one molecular proportion of Sodium Ethoxide.—The unsaturated keto-ester (IV, 18 g.) in absolute alcohol (10 c.c.) was added dropwise with shaking to a suspension of sodium ethoxide in absolute alcohol (prepared from 2.3 g. of sodium and 40 c.c. of anhydrous alcohol), cooled to below -5° by means of ice-salt mixture. An hour after the addition, the mixture was allowed to warm up to room temperature and kept overnight after which the product was worked up by acidifying with ice-cold dilute sulphuric acid and extraction with ether. The ethereal layer was washed twice with water and dried. After the removal of the solvent the residue on distillation in vacuum came over at $194^{\circ}/6$ mm., yield 11 g. The liquid did not respond to colour test with an alcoholic solution of ferric chloride. (Found : C, 59.78; H, 7.4. $C_{17}H_{26}O_7$ requires C, 59.64; H, 7.6 per cent).

Methylation in situ

In another lot with the same amount of materials as described in the previous experiment, the reaction mixture before being worked up was treated with 15 c.c. of methyl iodide and allowed to stand for 48 hours and then refluxed for 1 hour. After cooling, the product was diluted with water and extracted with ether and the ethereal layer washed and dried. The residue, left after evaporation of the solvent, on distillation in *vacuo* came over at $188^{\circ}/3$ mm., yield 7 g. (Found : C, 60.42; H, 7.6. $C_{18}H_{28}O_7$ requires C, 60.67; H, 7.86 per cent).

Attempted Methylation of the Malonic Ester derivative (V) with Methyl Iodide and molecularised Sodium in Benzene.—Sodium dust (2.5 g.) was taken under dry benzene and to it added the malonic ester derivative (V, 34 g.) with cooling; the mixture was allowed to stand overnight at room temperature when a gelatinous mass settled at the bottom. Methyl iodide (15 c.c.) was added and the mixture refluxed for 2 hours. After cooling and dilution with water, the solution was extracted with ether, the ethereal layer washed and dried. On distillation in *vacuo* a fraction came over at $80-100^{\circ}/6$ mm. Most probably this consisted mainly of ethyl methylmalonate. The residue could not be distilled. On attempted distillation even under 1 mm. it underwent profuse decomposition.

Condensation of Ethyl 2-Methyl- Δ^5 -cyclohexenone-2-carboxylate (IV) with Diethyl Methylmalonate.—Sodium (0.1 g.) was dissolved in 30 c.c. of absolute alcohol and cooled in ice. To this was added 18 g. of freshly distilled diethyl methylmalonate. After half an hour the solution was chilled to below -5° and the unsaturated keto-ester (IV, 18 g.) in 10 c.c. of absolute alcohol was added dropwise, the solution being shaken continuously during addition. The flask was allowed to stand in the ice-salt mixture for 2 hours and then warmed up to the room temperature and kept overnight. The

product was worked up by destroying the sodium ethoxide with a little acetic acid and after dilution with brine solution, the separated oil was extracted with ether. The ethereal extract was washed twice with water and dried. The residue, left after removal of the solvent, gave on distillation in *vacuo* only 4 g. of the desired product, b.p. $190^{\circ}/4$ mm. (Found : C, 60.56; H, 7.84. $C_{18}H_{28}O_7$ requires C, 60.67; H, 7.86 per cent).

Methylation of (V) with Sodium Ethoxide and Methyl Iodide.—To a solution of sodium ethoxide in alcohol (2.5 g. of clean cut sodium dissolved in 80 c.c. of anhydrous alcohol, and cooled to below -10° by ice-salt mixture) was added dropwise with shaking the malonic ester derivative (V, 34 g.) in 20 c.c. of anhydrous alcohol, when the solution gradually assumed a red colour; the reaction mixture was allowed to stand for $\frac{1}{2}$ hour in the freezing mixture, 25 c.c. of methyl iodide added in the cold, and the mixture was rapidly heated to boiling on a water-bath. The refluxing was continued for 4 hours, when the red colour of the solution mostly disappeared. The cooled solution was diluted with brine solution and extracted with ether, the ethereal layer washed with brine solution, water and dried. After evaporation of the solvent the residue was distilled in vacuum. The fraction (1.5 g.) of b.p. $80-90^{\circ}/6$ mm. consisting of ethyl methylmalonate and the fraction (29 g.) consisting of the desired product (VI). of b.p. $188^{\circ}/3$ mm. were obtained. (Found : C, 60.62; H, 7.82. $C_{18}H_{28}O_7$ requires C, 60.67; H, 7.86 per cent).

Ethyl 2-Methylcyclohexanone-5- α -propionate (VIII).—The keto-tricarboxylic ester (VI, 60 g.) was refluxed with 300 c. c. of concentrated hydrochloric acid for 36 hours. The solution was then evaporated in a basin and the residue taken up in ether and treated with dilute caustic soda solution; the solvent from the ethereal layer was evaporated and the residue subjected to hydrolysis with hydrochloric acid. The alkaline extract was acidified and extracted thrice with ether, the combined ethereal extract dried, the solvent removed and the residue evacuated at 5 mm. pressure for 1 hour. The dried acid weighing 25 g. was esterified by boiling with a mixture of 100 c. c. of absolute alcohol and 6 c. c. of concentrated sulphuric acid (d 1.84) for 12 hours. After diluting with cold water the solution was extracted with ether and the ethereal layer washed with sodium bicarbonate solution, water and then dried. After removal of the solvent from the dried ethereal extract, the residue was distilled in *vacuo*, when 22 g. of a clear, mobile liquid came over at $131^{\circ}/6.5$ mm. (Found : C, 67.68; H, 9.24. $C_{12}H_{20}O_3$ requires C, 67.92; H, 9.43 per cent).

The *semicarbazone* crystallised from dilute alcohol, m. p. 156° . (Found : N, 15.53. $C_{13}H_{23}O_3N_3$ requires N, 15.61 per cent).

cis-2-Methylcyclohexanol and its Dehydration.—2-Methylcyclohexanone (28 g.) was reduced with aluminium (5 g.) and isopropyl alcohol (80 c. c.) (*vide infra*). The residue after the usual working up of the reaction mixture gave on distillation 27 g. of the *cyclohexanol*, b. p. 167° . On dehydration with 70 g. of phosphorus pentoxide in dry benzene, as described later, it yielded 12 g. of methylcyclohexenones, b. p. 91° .

Oxidation of the Olefine mixture.—The above olefine mixture (12 g.) was oxidised with $KMnO_4$ (50 g. in 300 c. c. of water) at 0° for 34 hours with vigorous mechanical stirring. After filtration and extraction with ether, hydrochloric acid (conc., 65 c. c.) was added and the solution was saturated with ammonium sulphate and thoroughly

extracted with ether ten times. After drying with Na_2SO_4 , the ether was removed and the residue distilled in vacuum, when 5.5 g. of ϵ -keto-heptanoic acid, b. p. $165^\circ/12$ mm. was obtained. The *semicarbazone* was crystallised from aqueous alcohol, m. p. $142-43^\circ$ (mixed m. p. with an authentic specimen, $141-42^\circ$, cf. Price, *loc. cit.*).

Ethyl 2-Methylcyclohexanol-5- α -propionate (IX).—To aluminium isopropoxide (from 2 g. of aluminium, 25 c. c. of anhydrous isopropyl alcohol and 0.1 g. of mercuric chloride) were added the keto-ester (VIII, 20 g.) and anhydrous isopropyl alcohol (50 c. c.). The flask was attached to a fractionating column which in its turn was connected to a condenser. The mixture was slowly distilled for 8 to 9 hours, the vapours being kept at $60-70^\circ$. The remaining solvent was removed at a reduced pressure. The cooled reaction mixture was decomposed with ice-cold dilute sulphuric acid, extracted with ether, the ethereal layer washed and dried. After evaporation of the solvent, the residue on distillation in *vacuo* gave 18 g. of the desired hydroxy-ester (IX), b. p. $138^\circ/7$ mm. (Found: C, 67.10; H, 10.22. $\text{C}_{13}\text{H}_{22}\text{O}_4$ requires C, 67.28; H, 10.28 per cent).

Dehydration of the Hydroxy-ester (IX).—Phosphorus pentoxide (24 g., 2 mol.) was taken under dry benzene in a flask, cooled in ice-water and to this the hydroxy-ester (IX, 15 g.) was added slowly with shaking. The mixture assumed brownish colour. After standing for half an hour, the reaction mixture was heated on the water-bath for 2 hours. After cooling, the benzene layer was poured out of the flask and the dark brown gelatinous mass, which adhered to the bottom of the flask, decomposed with iced water and extracted with ether after addition of common salt to minimise emulsion. The ethereal extract, combined with the separated benzene solution, was washed with sodium bicarbonate solution and water and dried. After removal of the solvent from the ether-benzene mixture, the residue was distilled in *vacuo* when a clear liquid (7.6 g.) came over at $92^\circ-110^\circ$ (mainly at $105^\circ-108^\circ$). The liquid mixture was fractionated twice when two definite fractions were obtained, decolorising bromine solution in chloroform. Fraction (a) weighed 1.2 g., b. p. $95^\circ/7$ mm. (Found: C, 73.32; H, 10.26. $\text{C}_{13}\text{H}_{20}\text{O}_2$ requires C, 73.46; H, 10.2 per cent). The fraction (b) (X) weighed 5.2 g., b. p. $108^\circ/7$ mm. (Found: C, 73.26; H, 10.18. $\text{C}_{12}\text{H}_{20}\text{O}_2$ requires C, 73.46; H, 10.2 per cent).

β -(4-Methyl- Δ^3 -cyclohexenyl)-propyl Alcohol (XII).—The unsaturated ester (X, 30 g.) was dissolved in 225 c. c. of calcium-dried alcohol contained in a dry three-necked flask, connected with two condensers with guard tubes. The solution was warmed to 50° and to this was added 28 g. of clean-cut sodium all at once, when a vigorous reaction took place. Sometimes it was found necessary to cool the outer surface of the flask with a water-jet. After the initial vigour of the reaction had subsided, the flask was heated in an oil-bath at 180° until the whole of the sodium went into solution (3-4 hours). The reaction mixture was allowed to cool down to room temperature and 20 c. c. of water added and the mixture heated on the oil-bath (180°) for 1 hour. After cooling to about 50° , water (100 c. c.) was added to the solution and refluxing continued for 1 hour more. The reaction mixture after addition of some common salt to prevent frothing was steam-distilled, when ethyl alcohol came over rapidly and when it ceased to come, the residual liquor was cooled and extracted with ether and the ethereal layer washed with water and dried. After evaporation of ether, the residue was distilled in *vacuo* when the desired alcohol (XII) came over at $108^\circ/5$ mm. The liquid rapidly absorbed bromine

in chloroform solution, yield 16 g. (Found: C, 77.68; H, 11.42. $C_{10}H_{18}O$ requires C, 77.92; H, 11.68 per cent).

β -(4-Methyl- Δ^3 -cyclohexenyl)-propyl Bromide (XIII).—Phosphorus tribromide (3 c. c.) was added dropwise with shaking to 10 g. of the above alcohol (XII) and 1 c. c. of pyridine. During the addition the mixture was kept well cooled. After standing overnight the reaction mixture was heated on a water-bath for 15 minutes, cooled, decomposed with ice-cold dilute hydrochloric acid, extracted with ether, the ethereal layer washed and dried. The residue after removal of the ether was distilled in *vacuo* when the desired bromo compound (XIII) came over at 106–108°/6 mm., yield 8.5 g. (Found: Br, 36.48. $C_{10}H_{17}Br$ requires Br, 36.86 per cent).

β -Methylcrotononitrile.—(a). Dry acetone (32 g.) and cyanoacetic acid (30 g.) were taken in a flask cooled in ice-water, and to this were added dropwise with shaking 60 g. of freshly distilled piperidine, when a vigorous reaction took place. After $\frac{1}{2}$ hour the reaction mixture was heated in an oil-bath (100°–105°) for 2 hours. The cooled solution was acidified with ice-cold dilute hydrochloric acid and extracted with ether; the ethereal layer was washed and dried. After removal of the solvent, the residue was distilled when 24 g. of the nitrile came over at 142°.

(b). $\beta\beta$ -Dimethylacrylic acid was prepared according to Vogel's modification of Kohn's method starting from mesityl oxide. $\beta\beta$ -Dimethylacrylic acid (25 g.) was treated with 20 c. c. of thionyl chloride and allowed to stand overnight. After driving off the excess of thionyl chloride with the water-pump, the acid chloride was distilled, b.p. 122°, yield 23 g.

The acid chloride (23 g.) was added dropwise with shaking to well-cooled liquor ammonia (25 c. c.). After the addition the mixture was allowed to stand for 1 hour and diluted with 25 c. c. of water, filtered and crystals washed with 10 c. c. of cold water and dried, yield 16 g.

The above amide (16 g.) was mixed with phosphorus pentoxide (46 g.) and the mixture heated in an oil-bath (110°–115°) for 2 hours. After diluting the cooled mixture with ice-cold water, the solution was extracted with ether, the ethereal layer washed and dried. The residue, left after removal of the solvent, gave on distillation 6 g. of the nitrile, b.p. 142–43°.

Grignard Reaction between the Bromide (XIII) and β -Methylcrotononitrile.—Magnesium (2 g., 2 atoms) was dried in vacuum and taken in dry ether (10 c. c.) and to this was added 1 c. c. of methyl iodide to start the reaction. Maintaining the vigour throughout the reaction, 8 g. of the bromide (XIII) in 10 c. c. of dry ether were added drop by drop and the reaction mixture refluxed on the water-bath for 2 hours. During this period all the bromide reacted with magnesium. To the boiling Grignard solution was added β -methylcrotononitrile (5 g.) with shaking and then almost all the ether driven off. Dry thiophen-free benzene (10 c. c.) was added and refluxing continued for 12 hours, when a yellow Grignard complex of the ketimino compound settled at the bottom of the flask. Glacial acetic acid (20 c. c.) was added slowly to decompose the complex and the mixture heated for $\frac{1}{2}$ hour and water (40 c. c.) was then added and heating continued for 15 minutes. After extraction with ether the ethereal layer was washed, dried and the solvents driven off. The residue on fractionation in

vacuo gave 1.2 g. of the desired ketone (XV), b.p. $156^{\circ}/6$ mm. (Found: C, 81.62; H, 10.67. $C_{16}H_{24}O$ requires C, 81.8; H, 10.9 per cent).

β -Methylcrotonaldehyde.—Anhydrous hydrocyanic acid (5 c.c.) was poured at about -5° into freshly distilled quinoline (28 g., 0.2 mol.). On further cooling, a solution of the chloride of $\beta\beta$ -dimethylacrylic acid (10 g., 0.1 mol.) in 30 c.c. of absolute benzene was added through a dropping funnel during a period of 16 minutes. After standing at room temperature for about 20 hours, quinoline hydrochloride separated out. The reaction mixture was treated with 300 c.c. of ether and the resulting solution was successively washed three times with 20 c.c. of water, three times with 40 c.c. of 5N- H_2SO_4 , several times with 20 c.c. of saturated sodium bicarbonate solution until no further evolution of carbon dioxide occurred. It was then washed with 20 c.c. of distilled water and then dried over $CaCl_2$. After evaporation of the solvent 300 c.c. of 10N- H_2SO_4 were added to the residue and steam-distilled, the distillate being kept under nitrogen throughout the distillation. The distillate was then quickly extracted thrice with ether and the combined ethereal extracts washed with a little water and dried ($CaCl_2$). The residue left after removal of the ether was distilled in vacuum in an atmosphere of nitrogen, when 5.5 g. of the desired aldehyde passed over at $72^{\circ}/35$ mm. The *semicarbazone*, prepared in the usual way, melted at $216-18^{\circ}$ (lit. m.p., $220-21^{\circ}$). (Found: N, 30.2. $C_8H_{11}ON_3$ requires N, 29.79 per cent).

Zingiberene (I).—Magnesium (1 g.) was dried in vacuum and taken under 10 c.c. of dry ether and the reaction was started with 0.5 c.c. of ethyl iodide. The bromide (XIII, 5 g.) in 10 c.c. of dry ether was then added dropwise through a dropping funnel. The content of the flask was kept refluxing throughout the addition. After the formation of the Grignard compound was complete the flask was cooled in ice-water and β -methylcrotonaldehyde (5 g.) in 5 c.c. of dry ether was added with shaking. The reaction mixture was then kept overnight at room temperature. Next it was decomposed with ice and ammonium chloride, and the ethereal layer separated, washed with cold dilute sulphuric acid, sodium bicarbonate solution and water and then dried. After removing the solvent (ether) the residue was dried in vacuum (6 mm.) for 1 hour. It was then transferred to a 25 c.c. Claissen flask and to this was added 0.2 g. of *p*-toluene sulphonic acid. The mixture was then distilled under 6 mm. when a fraction (1.2 g.) was collected passing over at $112^{\circ}-130^{\circ}$. It was again fractionated when a few drops (about 0.4 g.) of the desired product came over at $118^{\circ}-122^{\circ}/6$ mm. (literature records b.p. $134^{\circ}/14$ mm.). It was only slightly brown in colour when freshly distilled but on standing the colour deepened. (Found: C, 87.9; H, 11.2. $C_{15}H_{22}$ requires C, 88.2; H, 11.76 per cent).

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APPLICATION OF MIXTURE LAW TO RHEOCHOR. PART I

By W. V. BHAGWAT AND M. V. SUBNIS

Mixture law has been applied to rheochor and mixtures of associated solutes in associated solvents have been studied. The values of R_x for acetone in acetic acid show a close agreement with R_{obs} observed, while in methyl alcohol and ethyl alcohol the straight line mixture law seems to hold. The agreement between R_x and R_{obs} for acetic acid is better in EtOH than in MeOH. The results for MeOH in ethyl alcohol also show that the mixture law is applicable. For the same solutes, the agreement between R_x and R_{obs} in different associated solvents is in the order: acetic acid > EtOH > MeOH. With increase of temperature, the values of R_x and R_{obs} fall and approach the R_{calc} , as it is the value at the boiling point of the liquid.

Friend (*Nature*, 1942, **140**, 432) suggested that in Sugden's parachor $\sigma^{\frac{1}{4}}$ may be substituted by $\eta^{\frac{1}{3}}$, where σ and η are the surface tension and viscosity respectively of the liquid. This gives

$$\frac{M\eta^{\frac{1}{3}}}{D} = \text{Constant} = R$$

where M is the molecular weight and D , the density of the liquid. The name 'Rheochor' was suggested for this constant. Friend (*loc. cit.*) observe that isomerides yield identical values of R . Bhagwat, Toshniwal and Moghe (*J. Indian Chem. Soc.*, 1944, **21**, 29) and Friend and Hargreaves (*Phil. Mag.*, 1943, *vii*, **34**, 643, 810; 1944; **35**, 57, 136, 619) have determined the values of atomic rheochor. Following are the values:—

C	... 12.8	Cl	... 27.3	N (—)	... 6.6
H in (C—H)	... 5.5	NH ₂	... 20.6		... 9.7
H in (O—H)	... 10.0	C ₆ H ₅ attached to alkyls	100.7	Br	... 36.0
O < (etheric)	... 10.0	, attached to other groups	102.7	(CO. acids and esters)	... 36.0
O = (ketonic)	... 13.2	Saturated six membered carbon ring	—5.6		
Co-valent bond	... 0.0	CN	... 33.0		
Co-ordinate bond	... -0.4	NH	... 13.6		

Bhagwat *et al.* (*loc. cit.*) tried to apply mixture law to rheochor. From the results (given in Chemists Year Book, 1937) they have shown that the law is applicable to sugar solutions. The work was extended by Bhagwat and Mandloi (*J. Indian Chem. Soc.*, 1946, **23**, 349) but no systematic work seems to have been done on these lines. Hammic and Andrew (*J. Chem. Soc.*, 1929, 754) have studied the application of mixture law to parachor. They have divided liquid mixtures into following groups: (i) Non-associated solutes in non-associated solvents, (ii) associated solutes in non-associated solvents and (iii) associated liquids in associated solvents. In all these cases they observed that for all concentrations of the solute the mixture law was applicable, but in all these cases the surface tensions of the

component liquids did not differ by more than 7 dynes/cm. For other liquid mixtures, where the difference was greater, the straight line mixture law was found to be applicable.

No results are given for water as a solvent, although they have concluded that the behaviour is anomalous. In the light of these observations for liquid-liquid mixtures in determining parachor, we thought it advisable to study the application of mixture law to rheochor on the same lines. Our results are given in the following pages.

EXPERIMENTAL

Viscosity of liquids and their mixtures was determined with the help of Ostwald's viscometer. Same viscometer and the same volume of liquids were used. The time for the flow of the liquid between two marks was noted by a stop-watch. The temperature was maintained constant between the limits $\pm 0.1^\circ$ by immersing the viscometer and the pyknometer in a thermostat regulated by electrical thermo-regulator. The density of the liquid or the mixture was determined with the help of a pyknometer. All the liquids used were 'A.R.' B.D.H. samples or Merck's samples and were distilled before use. If η_1 and η_2 are the viscosities of the liquid and the water respectively, d_1 and d_2 , their densities, and t_1 and t_2 , the time of fall between two marks, then $\eta_2/\eta_1 = d_2 t_2 / d_1 t_1$; the viscosity of water at a particular temperature is obtained from the standard tables and hence η_2 is calculated. The value so obtained is substituted in the expression

$$R = \frac{M(10^3 \eta)^{\frac{1}{3}}}{D + 2d}$$

As η is very small, $10^3 \eta$ is used. Further, d , the density of the substance in vapour state is very small. Hence the expression

$$R = \frac{M(10^3 \eta)^{\frac{1}{3}}}{D} \quad \text{is used. For liquid mixtures}$$

$$R_m = \frac{M_m (10^3 \eta)^{\frac{1}{3}}}{D}$$

where $M_m = (1-x)M + xM_x$ and $R_m = (1-x)R + xR_x$; M_m = mean molecular weight of the mixture, M = the molecular weight of the solvent, M_x = the molecular weight of the solute, R_m = the rheochor of the mixture, R = the rheochor of the solvent, R_x = the rheochor of the solute and x is the molar fraction of the solute in $(1-x)$ molecules of the solvent.

The liquids chosen were miscible in all proportions and hence the molar fraction of the solute was changed from 0 to 1. The results of viscosities obtained for standard liquids by the authors and those given in standard tables at the same temperature did not always agree, but since the same apparatus and liquids were used all throughout and that for establishing mixture law, comparison of experimental results alone was necessary; the point of identity between the results given in standard tables and those obtained by the authors was not much stressed. Further, in the expression $\eta^{\frac{1}{3}}$ is used so that even as high an error as 8% in η becomes only 1% in $\eta^{\frac{1}{3}}$.

Associated Liquids in Associated Solvents

TABLE I

Methyl alcohol in ethyl alcohol.

Temp. = 30°.

x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x .
0.000	0.7914	9.98	46.0	77.50	—
0.1388	0.7921	9.26	44.06	73.48	48.56
0.2516	0.7914	8.64	42.43	70.21	48.40
0.4752	0.7936	7.87	41.19	67.50	49.22
0.5707	0.7956	7.23	38.01	61.17	48.80
0.6891	0.7921	6.74	36.35	58.25	50.35
0.8384	0.7914	6.10	34.20	54.25	49.72
0.9272	0.7943	5.77	33.02	51.66	49.72
1.000	0.7969	5.60	32.0	—	—

 R_{calc} for methyl alcohol = 49.3 ; R_{obs} = 49.72.

The values of R_x shows that the mixture law is applicable, although at smaller concentrations of methyl alcohol the values are somewhat lower. No regular change is observed as the concentration is increased and the deviation from the observed value for pure methyl alcohol is within the experimental limits, since R_x is calculated from the mixture law,

$$R_m = (1-x) R + x R_x$$

and the error becomes more magnified, the smaller the value of x .

TABLE II

Acetic acid in ethyl alcohol.

Temp. = 30°.

x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x .
0.0	0.7989	10.14	46.00	77.69	—
0.1290	0.8260	10.56	47.80	77.69	77.96
0.1603	0.8335	10.67	48.27	77.78	78.00
0.3391	0.8820	11.34	50.75	77.93	78.50
0.5555	0.8399	12.09	53.78	78.12	78.50
0.7714	0.9926	12.26	56.80	78.25	78.45
0.8364	1.1009	11.99	57.73	78.21	78.30
1.0000	1.1040	10.52	60.00	—	77.47

 R_{calc} for acetic acid = 75.3 ; R_{obs} = 77.47.

Temp. = 40°.

x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x .
0.0000	0.7859	8.07	46.00	76.0	—
0.1290	0.8219	8.69	47.80	76.2	77.59
0.1603	0.8303	8.79	48.27	76.28	77.02
0.3391	0.8764	9.27	50.25	76.49	77.45
0.5555	0.9322	10.16	53.78	77.00	77.78
0.7714	0.9860	10.15	56.80	76.96	77.25
0.8364	1.1000	9.42	57.73	76.82	76.96
1.0000	1.1036	9.07	60.00	—	76.32

 R_{obs} = 76.32.

TABLE II (contd.)

Temp. = 50°.

x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x .
0.0000	0.7877	7.04	46.00	74.54	—
0.1290	0.8172	7.24	47.80	74.86	77.03
0.1603	0.8273	7.29	48.27	74.74	75.65
0.3391	0.8724	7.76	50.75	75.15	76.35
0.5555	0.9307	8.27	53.78	75.26	75.84
0.7714	0.9824	8.51	56.80	75.37	75.61
0.8364	0.9997	8.41	57.73	75.35	75.50
1.0000	1.1034	7.82	60.00	—	75.08

 $R_{obs} = 75.08$.

TABLE III

Acetic acid in methyl alcohol.

Temp. = 30°.

x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x .
0.0000	0.7969	5.60	32.00	49.72	—
0.2445	0.8828	7.55	38.84	56.78	78.57
0.4145	0.9330	8.83	43.61	61.37	77.84
0.6115	0.9779	11.08	49.12	67.84	79.38
0.7998	1.1015	11.68	54.39	72.85	78.56
1.0000	1.1040	10.55	60.00	—	77.47

Temp. = 40°.

x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x .
0.0000	0.7912	4.10	32.00	48.60	—
0.2445	0.8758	6.30	38.84	55.76	77.93
0.4145	0.9266	7.59	43.61	60.49	77.28
0.6115	0.9705	9.16	49.12	66.76	78.27
0.7998	1.1008	9.68	54.39	71.63	77.39
1.0000	1.1036	9.07	60.00	—	76.32

Temp. = 50°.

x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x .
0.0000	0.7880	3.99	32.00	47.97	—
0.2445	0.8694	5.48	38.84	55.26	77.84
0.4145	0.9215	6.62	43.61	59.94	76.86
0.6115	0.9620	7.76	49.12	65.97	77.43
0.7998	1.1003	8.20	54.39	70.50	76.14
1.0000	1.1034	7.82	60.00	—	75.08

TABLE IV

Acetone in acetic acid.

Temp. = 30°.

x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x .
0.0000	1.0410	10.730	60.0000	77.52	—
0.1907	0.9271	8.794	59.6186	79.25	86.62
0.3556	0.9410	7.338	59.2888	80.81	86.81
0.4737	0.9120	6.132	59.0526	81.23	85.98
0.6327	0.8707	5.055	58.7346	82.58	85.52
0.6336	0.8707	5.049	58.7328	82.58	85.49
0.8750	0.8111	3.862	58.2500	85.02	86.09
1.0000	0.7811	3.419	58.0000	—	86.58

 R_{calc} for acetone = 84.6, R_{obs} = 86.56.

TABLE IV (contd.)

Temp. = 40°.

x_m	$D.$	$\pi \times 10^3$	M_m	R_m	R_x
0.0000	1.0298	9.082	60.0000	76.83	—
0.1907	0.9771	7.501	59.6186	78.48	85.42
0.3556	0.9293	6.209	59.2888	80.15	86.22
0.4737	0.9016	5.426	59.0526	80.92	85.47
0.6327	0.8609	4.526	58.7345	82.35	85.53
0.6336	0.8609	4.508	58.7328	82.33	85.49
0.8750	0.8007	3.505	58.2500	85.09	86.27
1.0000	0.7705	3.116	58.0000	—	86.76

 $R'_{obs} = 86.76$

Temp. = 50°.

x_m	$D.$	$\pi \times 10^3$	M_m	R_m	R_x
0.0000	1.0183	7.785	60.0000	76.19	—
0.1907	0.9663	6.839	59.6186	78.43	87.93
0.3556	0.9183	5.461	59.2888	79.82	86.38
0.4737	0.8909	4.829	59.0526	80.69	85.68
0.6327	0.8497	4.070	58.7346	82.35	85.91
0.6336	0.8497	4.070	58.7328	82.35	85.90
0.8750	0.7889	3.212	58.2500	85.43	86.75
1.0000	0.7587	2.859	58.0000	—	87.16

 $R_{obs} = 86.76$

TABLE V

Acetone in methyl alcohol.

Temp. = 30°.

x_m	$D.$	$\eta \times 10^3$	M_m	R_m	R_x
0.0000	0.7921	5.745	32.0000	50.25	—
0.1135	0.7936	4.998	34.9510	53.84	82.02
0.1964	0.7932	4.450	37.1064	56.43	81.77
0.4456	0.7921	3.915	43.5856	65.25	83.90
0.6076	0.7889	3.667	47.7876	71.24	84.79
0.7939	0.7862	3.477	52.6414	78.23	85.50
0.9136	0.7838	3.426	55.9536	83.26	86.38
1.0000	0.7811	3.394	58.0000	—	86.48

Temp. = 40°.

x_m	$D.$	$\eta \times 10^3$	M_m	R_m	R_x
0.0000	0.7839	5.148	32.0000	50.08	—
0.1135	0.7844	4.552	34.9510	53.84	83.25
0.1964	0.7825	4.227	37.1064	56.76	84.11
0.4456	0.7829	3.627	43.5856	65.39	84.44
0.6076	0.7785	3.419	47.7876	71.55	85.41
0.7939	0.7750	3.179	52.6414	78.42	85.81
0.9136	0.7719	3.108	55.9536	83.51	86.67
1.0000	0.7705	3.082	58.0000	—	86.64

Temp. = 50°.

x_m	$D.$	$\eta \times 10^3$	M_m	R_m	R_x
0.0000	0.7750	4.327	32.0000	49.69	—
0.1135	0.7754	3.869	34.9510	53.37	82.20
0.1964	0.7723	3.620	37.1064	56.43	84.01
0.4456	0.7682	3.154	43.5856	65.48	85.12
0.6076	0.7672	3.004	47.7876	71.45	85.50
0.7939	0.7638	2.888	52.6414	78.66	86.18
0.9136	0.7609	2.810	55.9536	83.66	87.97
1.0000	0.7587	2.803	58.0000	—	86.94

TABLE VI

Acetone in ethyl alcohol.

Temp. = 30°.					
x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x
0.0000	0.7919	10.610	46.0000	78.05	—
0.1622	0.7909	7.565	47.9464	78.23	79.16
0.2894	0.7895	5.917	49.4728	78.23	78.64
0.6712	0.7848	3.931	54.0544	81.36	82.98
0.7382	0.7842	3.794	54.8584	82.62	84.24
0.8267	0.7840	3.775	55.9204	84.22	85.50
1.0000	0.7811	3.360	58.0000	—	86.38

Temp. = 40°.					
x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x
0.0000	0.7827	8.414	46.0000	76.70	—
0.1622	0.7825	6.316	47.9464	77.13	79.40
0.2894	0.7803	5.089	49.4728	77.67	80.09
0.6712	0.7756	3.565	54.0544	81.70	84.13
0.7382	0.7750	3.452	54.8584	82.62	84.73
0.8267	0.7737	3.297	55.9204	83.89	85.39
1.0000	0.7713	3.137	58.0000	—	86.72

Temp. = 50°.					
x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x
0.0000	0.7746	6.993	46.0000	75.39	—
0.1622	0.7740	5.335	47.9464	76.37	81.44
0.2894	0.7705	4.398	49.4728	77.25	81.78
0.6712	0.7633	3.213	54.0544	81.93	85.13
0.7382	0.7615	3.103	54.8584	82.96	85.62
0.8267	0.7597	2.942	55.9204	84.24	86.10
1.0000	0.7578	2.840	58.0000	—	87.18

The values of R_x for acetic acid in ethyl alcohol at all temperatures show a close agreement with R_{obs} for acetic acid at the corresponding temperatures. The value of R_x falls with temperature, so also the value of R_{obs} and both show better agreement with the calculated values at higher temperatures. This is as is expected, since R_{calc} always corresponds to the boiling point temperature of the liquid. The values of R_x for acetic acid in methyl alcohol show a similar behaviour.

The results with acetone in acetic acid show a close agreement between R_{obs} and R_{calc} for all concentrations. R_{obs} at different temperatures examined by us does not show much variation with temperature, since the temperatures examined are not far removed from the boiling point of acetone.

In the cases of methyl alcohol and ethyl alcohol, as solvents for acetone, the R_{obs} and R_x do not agree at all concentrations. The values which are low at lower concentrations increase steadily with increase in the concentration of acetone. In short, it seems that the straight line mixture law is applicable.

NITRATION OF SOME COUMARIN DERIVATIVES

By A. R. NAIK AND G. V. JADHAV

7-Hydroxy-4-methylcoumarin, its methyl ether, 7-hydroxy-4-methylcoumarin-6-carboxylic acid and its methyl ester have been nitrated and their nitro derivatives obtained.

Pechmann and Obermiller (*Ber.*, 1901, **34**, 666) claimed to have obtained 7-hydroxy-4-methyl-8-nitrocoumarin by nitrating 7-hydroxy-4-methylcoumarin at 0° but the nitro product obtained in this work had a considerable lowering in melting point with an authentic specimen, prepared according to Chakravarti and Ghosh (*J. Indian Chem. Soc.*, 1935, **12**, 622). They also claim to have obtained dinitro compound but all attempts to prepare the same proved unsuccessful. No literature is available on the nitration of 7-hydroxy-4-methylcoumarin-6-carboxylic acid and its methyl ester.

7-Hydroxy-4-methylcoumarin on nitration under one set of conditions gives a nitro derivative melting at 253° , identical with 7-hydroxy-4-methyl-6-nitrocoumarin, prepared by Chakravarti and Banerji (*J. Indian Chem. Soc.*, 1937, **14**, 37) and a trinitro derivative under different conditions, whereas the nitration of its methyl ether under similar conditions gives the nitro derivatives of the methyl ether.

Nitration of 7-hydroxy-4-methylcoumarin-6-carboxylic acid gives dinitro and trinitro derivatives, whereas the methyl ester of the same under different conditions gives mono-nitro and dinitro derivatives only. The constitution of these compounds has been established.

EXPERIMENTAL

7-Hydroxy-4-methyl-6-nitrocoumarin.—A mixture of nitric acid ($d\ 1.42$, 2 c.c.) and sulphuric acid (6 c.c.) was added drop by drop to the well stirred and ice-cooled sulphuric acid solution (40 c.c.) of 7-hydroxy-4-methylcoumarin (5 g.). After the addition was complete, the reaction mixture was kept at $5-10^{\circ}$ for about 30 minutes and then poured over crushed ice, when yellow flakes separated. The crude product after crystallisation from acetic acid melted at 253° . (Found: N, 6.5. $C_{10}H_7O_5N$ requires N, 6.3 per cent). Mixed m.p. with an authentic specimen showed no lowering.

7-Methoxy-4-methyl-6-nitrocoumarin.—7-Methoxy-4-methylcoumarin (1 g.), suspended in acetic acid (20 c.c.) was treated with nitric acid ($d\ 1.42$, 4 c.c.) and the reaction mixture was kept on a boiling water-bath for about 30 minutes. When cold, the solution gave some yellow needles, m.p. 282° . The mother-liquor gave more solid on dilution. (Found: N, 6.1. $C_{11}H_9O_5N$ requires N, 5.95 per cent).

The same compound was obtained by methylating the above hydroxy-nitrocoumarin in dry acetone solution with methyl iodide in presence of anhydrous potassium carbonate and by boiling for 20 hours. The solid obtained after removal of the liquids was first washed with 2% solution of caustic soda and then crystallised from acetic acid.

This nitro derivative was heated with anhydrous aluminium chloride at 150° - 160° for about 3 hours and then the mixture was treated with dilute hydrochloric acid and filtered. The solid was extracted with a 4% solution of sodium hydroxide and crystallised from acetic acid, m.p. 253° . It was found identical with 7-hydroxy-4-methyl-6-nitro-coumarin (mixed m.p.).

7-Hydroxy-4-methyl-3:6:8-trinitrocoumarin.—7-Hydroxy-4-methylcoumarin (5 g.) was suspended in acetic acid (50 c.c.) and nitric acid (d 1.42, 20 c.c.) was gradually added to it. The reaction mixture was heated on a boiling water-bath for about 15 minutes. On cooling, yellow cubes separated, m.p. 225 - 26° (decomp.). (Found: N, 13.8. $C_{10}H_5O_9N_3$ requires N, 13.5 per cent).

The same substance was also obtained by allowing the above mixture to remain at room temperature for about 24 hours.

2:4-Dihydroxy-3:5-dinitroacetophenone.—The above trinitrocoumarin (1 g.) was heated with liquor ammonia on a boiling water-bath for about 2 hours. The orange solution was acidified after cooling, filtered, and the filtrate extracted with ether. The solid obtained after removal of the ether was crystallised from methyl alcohol, m.p. 168 - 69° . (Found: N, 11.7. $C_8H_6O_7N_2$ requires N, 11.6 per cent). Mixed melting point with an authentic specimen of 2:4-dihydroxy-3:5-dinitroacetophenone showed no lowering.

7-Methoxy-4-methyl-3:6:8-trinitrocoumarin.—7-Methoxy-4-methylcoumarin (1 g.) was nitrated in sulphuric acid solution (10 c.c.) by using a mixture of nitric acid (4 c.c., d 1.42) and sulphuric acid (4 c.c.) at 5 - 10° for about half an hour, when a small quantity of a crystalline substance separated. More solid was obtained when the mixture was poured over crushed ice. It crystallised from acetic acid in yellow needles, m.p. 180 - 81° . (Found: N, 13.1. $C_{11}H_7O_9N_3$ requires N, 12.9 per cent).

Demethylation with 30% solution of hydrobromic acid in acetic acid, by heating at 140 - 50° for about 2 hours, gave the corresponding hydroxy compound.

Methyl 7-Hydroxy-4-methyl-8-nitrocoumarin-6-carboxylate.—Methyl 7-hydroxy-4-methylcoumarin-6-carboxylate (5 g.) was suspended in acetic acid (75 c.c.) and nitric acid (d 1.42, 40 c.c.) was added to it dropwise, when the ester gradually went into solution and after some time crystals began to separate. After 3 hours the flask was cooled in ice for some time and the solid filtered. It crystallised from acetic acid in pale yellow needles, m.p. 256 - 57° . Some more substance was obtained from the mother-liquor on dilution. (Found: N, 5.2. $C_{12}H_9O_7N$ requires N, 5.02 per cent).

Hydrolysis.—(a). The above substance was hydrolysed by boiling with 20% sodium hydroxide solution (40 c.c.) for about 4 hours, acidified with hydrochloric acid and then steam-distilled, when the nitro compound was obtained which crystallised from alcohol in orange needles, m.p. 85° (mixed m.p. with 2-nitroresorcinol).

(b). When it was hydrolysed with 20% sodium hydroxide (40 c.c. for 1 g.) at room temperature for about 3 days, it gave 7-hydroxy-4-methyl-8-nitrocoumarin-6-carboxylic acid, which crystallised from acetic acid in pale yellow needles, m.p. 288° (decomp.). It gave a violet colour with alcoholic ferric chloride. It is sparingly soluble in alcohol, acetic acid and insoluble in benzene, carbon tetrachloride and water. (Found: N, 5.5. $C_{11}H_7O_7N$ requires N, 5.3 per cent).

Hydrolysis with sulphuric acid (5 c.c.) in glacial acetic acid (40 c.c. for 1 g.) by boiling for 3 hours gave the same acid. The acid was esterified to the original ester by boiling with methyl alcohol in presence of sulphuric acid for 16 hours.

Methyl 7-Methoxy-4-methyl-8-nitrocoumarin-6-carboxylate.—Sodium salt of methyl 7-hydroxy-4-methyl-8-nitrocoumarin-6-carboxylate was prepared by dissolving it in absolute alcohol and then adding 25% solution of sodium hydroxide, when the salt separated. It was filtered, washed with absolute alcohol and dried at 160°.

The dry salt (1 g.) was suspended in dry toluene (30 c.c.), dimethyl sulphate (1.5 c.c.) added and the mixture refluxed at 120° for 6 hours. Toluene was removed by steam-distillation and the residue was washed with dilute sodium hydroxide solution and then with water. It crystallised from methyl alcohol in pale yellow needles, m.p. 189-90°. It is soluble in methyl alcohol, ethyl alcohol, acetic acid and benzene. (Found: N, 4.5. $C_{13}H_{11}O_7N$ requires N, 4.8 per cent).

Methyl 7-Acetoxy-4-methyl-8-nitrocoumarin-6-carboxylate.—The hydroxy compound (1 g.) was heated at 140°-145° with acetic anhydride (7 c.c.) and pyridine (2-3 drops) for about 4 hours. It was then diluted with ice-cold water when a pasty mass was obtained which slowly solidified on standing at room temperature. It crystallised from acetic acid in shining white needles, m.p. 222-23°. (Found: N, 4.5. $C_{14}H_{11}O_8N$ requires N, 4.4 per cent).

Methyl 7-Hydroxy-4-methyl-3:8-dinitrocoumarin-6-carboxylate—(a). Nitric acid (d 1.42, 20 c.c.) was gradually added to methyl 7-hydroxy-4-methylcoumarin-6-carboxylate (5 g.), suspended in acetic acid (50 c.c.) and the mixture heated on a boiling water-bath for about an hour. Some yellow cubes separated on cooling the reaction mixture, which melted at 246-47° (decomp.). Dilution of the mother-liquor with water gave a further amount of the compound. It gave a reddish coloration with alcoholic ferric chloride. It is sparingly soluble in methyl alcohol, ethyl alcohol and acetic acid. (Found: N, 8.7. $C_{12}H_8O_9N_2$ requires N, 8.6 per cent).

(b). It was also obtained when nitration of the ester (1 g.) in acetic acid (15 c.c.) with nitric acid (d 1.42, 8 c.c.) was allowed to proceed at room temperature for 3 days. (After 3 hours the mono-nitro compound first separated which slowly went into solution and finally the required substance separated).

(c). A mixture of nitric acid (4 c.c.) and sulphuric acid (4 c.c.) was added to the ester (1 g.), dissolved in sulphuric acid (8 c.c.) and surrounded by ice. The reaction mixture was left at room temperature for about 30 minutes and then poured over crushed ice, when the dinitro compound was obtained.

Methyl 7-Acetoxy-4-methyl-3:8-dinitrocoumarin-6-carboxylate.—The above dinitro ester was acetylated with acetic anhydride in presence of pyridine yielding pale yellow cubes, m.p. 198-99°. (Found: N, 7.8. $C_{14}H_{10}O_{10}N_2$ requires N, 7.7 per cent).

2:4-Dihydroxy-3-nitro-5-carbomethoxyacetophenone.—Methyl-7-hydroxy-4-methyl-3:8-dinitrocoumarin-6-carboxylate (5 g.) was boiled with liquor ammonia (200 c.c.) until all ammonia was driven out. When cold, the reaction mixture was acidified and the precipitate obtained was repeatedly crystallised from dilute alcohol, m.p. 194-95°. It gave a red coloration with alcoholic ferric chloride. (Found: N, 5.8. $C_{16}H_{10}O_7N$ requires N, 5.5 per cent).

2:4-Dihydroxy-3-nitro-5-carboxy-acetophenone.—The above compound was hydrolysed by heating on a boiling water-bath with 8% sodium hydroxide (20 c.c.) for about an hour. It crystallised from water, acidified with a few drops of hydrochloric acid, in tiny needles, m.p. 242-43°. It is very soluble in methyl alcohol, ethyl alcohol, acetic acid and sparingly soluble in benzene and chloroform. (Found: N, 5.9. $C_9H_7O_7N$ requires N, 5.8 per cent). The phenylhydrazone was obtained in yellow needles from acetic acid, m.p. 258-59°. (Found N, 12.3. $C_{18}H_{13}O_6N_3$ requires N, 12.2 per cent).

2:4-Dihydroxy-3-nitro-acetophenone.—The above compound was heated in a sealed tube at 140-145° for about 10 hours with water (7 c.c.), acetic acid (5 c.c.) and hydrochloric acid (5 c.c.). The reaction mixture was then extracted with ether. The residue after removal of the ether was left in an alkaline desiccator and the solid finally crystallised from alcohol in yellow needles, m.p. 93°. (Found: N, 7.3. $C_8H_7O_6N$ requires N, 7.1 per cent). (Mixed m.p. with a genuine specimen).

7-Hydroxy-4-methyl-3:8-dinitrocoumarin-6-carboxylic Acid.—Sulphuric acid (5 c.c.) was added to the solution of methyl 7-hydroxy-4-methyl-3:8-dinitrocoumarin-6-carboxylate (1 g.) in acetic acid (20 c.c.) and boiled for 3 hours. Yellow needles separated on cooling the solution. It crystallised from alcohol, m.p. 275-76° (decomp.). (Found: N, 8.9. $C_{11}H_8O_8N_2$ requires N, 9.03 per cent).

It was esterified to the original ester by boiling it with methyl alcohol in presence of sulphuric acid for 16 hours.

7-Hydroxy-4-methyl-6:8-dinitrocoumarin.—Fuming nitric acid (d 1.5, 30 c.c.) was gradually added to 7-hydroxy-4-methylcoumarin-6-carboxylic acid (5 g.), suspended in acetic acid (75 c.c.) when a considerable rise in temperature took place. After 15 minutes, small crystals began to separate. The mixture was cooled in ice and the solid filtered, washed with water and crystallised from acetic acid in yellow cubes, m.p. 291-92° (decomp.). It is sparingly soluble in acetic acid, insoluble in benzene, chloroform and carbon tetrachloride. (Found: N, 10.6. $C_{10}H_8O_7N_2$ requires N, 10.7 per cent).

7-Hydroxy-4-methyl-3:6:8-trinitrocoumarin.—7-Hydroxy-4-methylcoumarin-6-carboxylic acid (1 g.), suspended in acetic acid (10 c.c.) was treated with fuming nitric acid (8 c. c.) as above, but the reaction was allowed to proceed for 4 days, when crystals first formed redissolved and new crystals were formed. It crystallised from acetic acid in yellow cubes, m. p. 225-26°. (Found: N, 13.7. $C_{10}H_5O_8N_3$ requires N, 13.5 per cent).

The substance was also obtained by nitrating 7-hydroxy-4-methyl-3:8-dinitro-6-carboxylic acid with fuming nitric acid in acetic acid solution for about 4 days as well as from 7-hydroxy-4-methylcoumarin.

ORGANIC CHEMISTRY DEPARTMENT,
ROYAL INSTITUTE OF SCIENCE, BOMBAY
AND
KARNATAK COLLEGE, DHARWAR.

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GROUP PARACHORS BY GIBLING'S METHOD. PART I

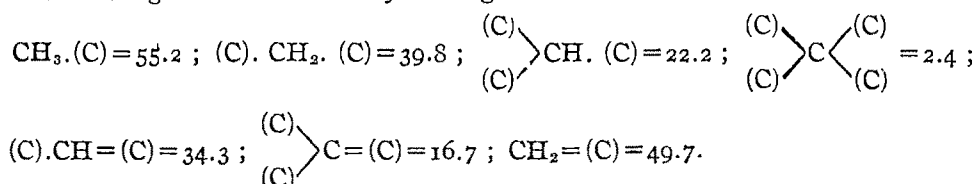
BY W. V. BHAGWAT AND G. V. BAKORE

The group parachors (C).CH₂.NH₂=83.4, (C).CH₂Cl=95.6, (C).CH₂.Br=108.7 and (C).CH₂.I=130.1, have been determined. They have been shown to reproduce experimental results better than Sugden's values. However, it seems that even group parachors are modified by the length of the chain of carbon atoms and also by side chains.

Gibling (*J. Chem. Soc.*, 1941, 299) has suggested a new method of evaluating structural parachors. According to him it is more accurate to substitute group parachors for atomic parachors and structural constants. However, his work was limited to carbon, hydrogen and oxygen atoms and that too, to aliphatic compounds. Bhagwat and Shukla (*J. Indian Chem. Soc.*, 1945, 22, 115, 222) have extended this work to aromatic compounds and have determined the values for benzene ring and other groups in aromatic substances. The structural parachors of several other groups, both aromatic and aliphatic, still remain to be determined and unless these values are made known, it is impossible to utilise Gibling's method for the investigation of the unknown or doubtful structures. We have therefore tried to determine the structural parachor of as many groups as possible from the available data. The results used are those given in the list of parachors by British Association for the Advancement of Science (1932).

Structural Parachor of C. CH₂. NH₂ group.

Following structural values by Gibling have been used :



For benzene ring the value = 0, as given by Bhagwat and Shukla (*loc. cit.*), is employed.

In order to determine the parachor of a particular group, several compounds containing that group were taken and their standard values (S. V.) were obtained by subtracting expansion corrections (E. C.) from the observed parachors. When parachors of various groups, except of the group whose parachor is required, are subtracted from the S. V., the group parachor is obtained. The method is illustrated by the following example.

Ethylamine (CH₃.CH₂.NH₂) : $P_{\text{obs}} = 137.4$. E.C. = 0.2.

Hence $S.V. = 137.4 - 0.2 = 137.2$. CH₃.(C) = 55.2.

Hence group parachor for (C).CH₂.NH₂ = 137.2 - 55.2 = 82.0

Table II illustrates that the values calculated by structural parachor method show much better agreement with the experimental values than with the values calculated by Sugden's method.

TABLE I

Compound.	$P_{\text{obs.}}$	E. C.	Groups subtracted.	P for (C).CH ₂ .NH ₂
Ethylamine CH ₃ -CH ₂ .NH ₂	137.4	0.2	CH ₃ -(C)	82.0
<i>n</i> -Propylamine CH ₃ -(CH ₂) ₂ .NH ₂	178.5	0.3	CH ₃ -(C) and (C)-CH ₂ -(C)	83.2
<i>iso</i> Butylamine $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \\ \diagdown \\ \text{CH}_3 \end{array}$ CH ₂ .NH ₂	216.1	0.3	2 CH ₃ -(C) and (C) $\begin{array}{c} \diagup \\ \diagdown \end{array}$ CH-(C)	83.2
<i>ter</i> -Amylamine $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CH}_3 \end{array}$ CH ₂ .NH ₂	252.3	0.5	3 CH ₃ -(C) and (C) $\begin{array}{c} \diagup \\ \diagdown \end{array}$ C $\begin{array}{c} \diagup \\ \diagdown \end{array}$ (C)	83.8
Benzylamine C ₆ H ₅ .CH ₂ .NH ₂	273.7	0.7	5 (C)-CH ₂ -(C) and (C) $\begin{array}{c} \diagup \\ \diagdown \end{array}$ C=(C)	84.8
				Mean 83.4

TABLE II

Compound	P (Structural method)	$P_{\text{obs.}}$	P (Sugden's method).
Ethylamine	133.8	137.4	141.8
<i>n</i> -Propylamine	178.7	178.5	180.8
<i>iso</i> Butylamine	216.3	216.1	219.8
<i>ter</i> -Amylamine	251.9	252.3	258.8
Benzylamine	272.3	273.7	275.7

TABLE III

Group parachor for (C)-CH₂.Cl

Compound.	$P_{\text{obs.}}$	E. C.	Groups subtracted.	P for (C).CH ₂ .Cl
Ethyl chloride CH ₃ -CH ₂ .Cl	151.6	0.2	CH ₃ -(C)	96.2
<i>n</i> -Propyl chloride CH ₃ -CH ₂ -CH ₂ .Cl	190.2	0.3	CH ₃ -(C) and (C)-CH ₂ -(C)	94.9
<i>n</i> -Butyl chloride CH ₃ -(CH ₂) ₂ .CH ₂ .Cl	230.5	0.5	CH ₃ -(C) and 2 (C)-CH ₂ -(C)	95.2
<i>iso</i> Butyl chloride $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \\ \diagdown \\ \text{CH}_3 \end{array}$ CH ₂ .Cl	228.4	0.5	2 CH ₃ -(C) and (C) $\begin{array}{c} \diagup \\ \diagdown \end{array}$ CH-(C)	95.3
<i>n</i> -Amyl chloride CH ₃ -(CH ₂) ₃ .CH ₂ .Cl	270.4	0.7	CH ₃ -(C) and 3 (C)-CH ₂ -(C)	95.1
<i>iso</i> Amyl chloride $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CH}_3 \end{array}$ CH ₂ .CH ₂ .Cl	269.8	0.7	2 CH ₃ -(C), (C) $\begin{array}{c} \diagup \\ \diagdown \end{array}$ CH-(C) and (C)-CH ₂ -(C)	96.7
				Mean 95.6

The values obtained from the structural method and those from Sugden's method are compared with the observed parachor values in Table IV. Structural parachor method shows better agreement with the experimental values.

TABLE IV

Compound.	<i>P</i> (Structural method).	<i>P</i> _{obs.}	<i>P</i> (Sugden's method).
Ethyl chloride	151.0	151.6	149.4
<i>n</i> -Propyl chloride	190.9	190.2	188.4
<i>n</i> -Butyl chloride	230.9	230.5	227.4
<i>iso</i> Butyl chloride	228.7	228.4	227.4
<i>n</i> -Amyl chloride	270.9	270.4	266.4
<i>iso</i> Amyl chloride	268.7	269.8	266.4

TABLE V

Group parachor for (C)—CH₂. Br

Compound.	<i>P</i> _{obs.}	E. C.	Groups subtracted.	<i>P</i> for (C)—CH ₂ —Br
Ethyl bromide CH ₃ —CH ₂ . Br	165.7	0.2	CH ₃ —(C)	110.3
<i>n</i> -Propyl bromide CH ₃ —CH ₂ —CH ₂ . Br	205.3	0.4	CH ₃ —(C) and (C)—CH ₂ —(C)	109.9
<i>n</i> -Butyl bromide CH ₃ —(CH ₂) ₂ —CH ₂ . Br	243.5	0.6	CH ₃ —(C) and 2 (C)—CH ₂ —(C)	108.1
<i>iso</i> Butyl bromide CH ₃ —CH(CH ₃)—CH ₂ . Br	243.8	0.6	2 CH ₃ —(C) and (C)—CH—(C)	110.6
<i>n</i> -Amyl bromide CH ₃ —(CH ₂) ₃ —CH ₂ . Br	283.6	0.8	CH ₃ —(C), 3 (C)—CH ₂ —(C)	108.2
<i>iso</i> -Amyl bromide CH ₃ —CH(CH ₃)—CH ₂ —CH ₂ . Br	282.9	0.8	2 CH ₃ —(C), (C)—CH ₂ —(C) and (C)—CH—(C)	109.7
<i>n</i> -Hexyl bromide CH ₃ —(CH ₂) ₄ —CH ₂ . Br	322.8	1.0	CH ₃ —(C) and 4 (C)—CH ₂ —(C)	107.4
<i>n</i> -Heptyl bromide CH ₃ —(CH ₂) ₅ —CH ₂ . Br	363.0	1.2	CH ₃ —(C) and 5 (C)—CH ₂ —(C)	107.6
<i>n</i> -Octyl bromide CH ₃ —(CH ₂) ₆ —CH ₂ . Br	402.4	1.5	CH ₃ —(C) and 6 (C)—CH ₂ —(C)	106.9
			Mean	108.7

The parachor values obtained from structural method and from Sugden's method are compared with the observed values. The structural values are in better agreement with the observed values compared to Sugden's method (Table VI).

TABLE VI

Compound.	Parachor values (<i>P</i>)		
	Structural method.	Observed.	Sugden's method.
Ethyl bromide	164.1	165.7	163.1
<i>n</i> -Propyl bromide	204.1	205.3	202.1
<i>n</i> -Butyl bromide	244.1	243.5	241.1
<i>iso</i> Butyl bromide	241.9	243.8	241.1
<i>n</i> -Amyl bromide	284.1	283.6	280.1
<i>iso</i> Amyl bromide	281.9	282.9	280.1
<i>n</i> -Hexyl bromide	324.1	322.8	319.1
<i>n</i> -Heptyl bromide	364.1	363.0	358.1
<i>n</i> -Octyl bromide	404.2	402.4	397.1

TABLE VII

Group parachor for (C)—CH₂—I.

Compound.	<i>P</i> obs.	E. C	Groups subtracted.	<i>P</i> for (C)—CH ₂ . I.
Ethyl iodide CH ₃ —CH ₂ I	187.0	0.3	CH ₃ —(C)	131.5
<i>n</i> -Propyl iodide CH ₃ —CH ₂ —CH ₂ I	226.0	0.5	CH—(C) and (C)—CH ₂ —(C)	130.5
<i>n</i> -Butyl iodide CH ₃ —(CH ₂) ₂ —CH ₂ I	264.7	0.7	CH ₃ —(C) and 2 (C)—CH ₂ —(C)	129.2
<i>iso</i> Butyl iodide $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} \\ \diagup \\ \text{CH}_3 \end{array} \text{—CH}_2 \text{ I}$	265.0	0.7	2 CH ₃ —(C), $\begin{array}{c} \text{(C)} \\ \diagdown \\ \text{CH} \\ \diagup \\ \text{(C)} \end{array}$ —CH ₂ —(C)	131.7
<i>n</i> Hexyl iodide CH ₃ —(CH ₂) ₄ —CH ₂ I	344.1	1.1	CH ₃ —(C), 4(C)—CH ₂ —(C)	128.6
<i>n</i> Heptyl iodide CH ₃ —(CH ₂) ₅ —CH ₂ I	384.5	1.5	CH ₃ —C, 5(C)—CH ₂ —(C)	128.8
				Mean 130.05 or 130.1

The structural parachor values and those obtained from Sugden's method are compared with those of the observed values (Table VIII).

TABLE VIII

Compound.	Parachor values (<i>P</i>)		
	Structural.	Observed	Sugden's.
Ethyl iodide	185.6	187.0	186.1
<i>n</i> -Propyl iodide	225.6	226.0	225.1
<i>n</i> -Butyl iodide	265.6	264.7	264.1
<i>iso</i> Butyl iodide	263.4	265.0	264.1
<i>n</i> -Hexyl iodide	345.6	344.1	342.1
<i>n</i> -Heptyl iodide	385.8	384.5	381.1

In spite of the better results obtained by Gibling's method it has to be noted that the group parachor does not seem to be a true constant, but varies in the same homologous series as we pass from one member to another. Thus, the value of (C)—CH₂—NH₂ group continuously increases as the number of carbon atoms in the chain increases. In case of alkyl chlorides same is true for (C)—CH₂—Cl, although the first member, ethyl chloride shows anomalous behaviour. On the other hand, the value for (C)—CH₂—Br group from alkyl bromide falls as we ascend the series. The first member, ethyl bromide and *iso*-butyl bromide with branch chain show anomalous behaviour. The observations for (C)—CH₂—I group from alkyl iodide are very similar to those of (C)—CH₂—Br group.

QUALITY OF IRRIGATION WATER. EFFECT ON p_H VALUE AND EXCHANGEABLE BASES OF SOILS

By A. G. ASGHAR AND C. L. DHAWAN

Irrigation water containing sodium salts even within permissible limits would produce a slow deterioration on good soil.

A negative salt index of a water-sample is a useful and safe indication of its suitability for irrigation purposes. The waters with positive salt indices would produce slow deterioration in the soil, while waters with negative salt indices may even be used for reclamation purposes.

Sodium salts in the irrigation water increase the p_H value and the exchangeable sodium and potassium of the soil. A corresponding decrease in the exchangeable calcium is also brought about with the consequent lowering of the fertility of the soil.

Treatment of bad irrigation waters can be effected by the addition of gypsum or calcium permutite.

The p_H value and the total salt contents of a soil are the two important factors which must be carefully controlled in soil treatment. Taylor (*Indian Farming*, 1940, 1, 424) has laid down limits of fertility and deterioration of soils in relation to their p_H and total salt content. The conclusion drawn from this study is that if the salt content of the soil exceeds 0.2% or the alkalinity exceeds p_H value of 8.5, then soil deterioration has commenced and the crop yields will be below the normal. In addition to these factors, exchangeable bases have also been considered to be an index of fertility.

There are two points to be considered in this connection. When saline water is used for irrigation purpose, salts are added to the soil. Even if the salt concentration is very low and a part of the salt is removed by plants, there is likely to be a gradual accumulation of salts, which may produce 'Thur' in the long run, and ultimately the soil may become alkaline and reach the final stage of deterioration. The second point is the immediate effect of salts on plant growth, as all the plants cannot resist the effect of salts to the same extent.

Kelly (*Trans. Amer. Soc. Civ. Eng.*, 1941, Vol. 106) has mentioned the pioneer work of Hilgard, Forbes, and Schofield; but he has not laid down limits of suitability of irrigation waters. Puffles (*Soil Sci.*, 1939, 47, 447) while studying the effect of saline water on loess soils has concluded that a saline water possessing a high concentration of sodium salts, as compared with calcium salts, would eventually turn the soil useless for agricultural purposes. Taylor, Puri and Asghar (Memoir, Punjab Irrigation Research, 1935, Vol. IV, No 9) have expressed the following empirical formula for specifying the quality of an irrigation water. All quantities in this formula refer to parts per hundred thousand.

$$\text{Salt index} = (\text{Total Na} - 24.5) - (\text{total Ca} - \text{Ca in CaCO}_3 \times 4.85).$$

The salt index is negative for all good waters and positive for those unsuitable for irrigation purposes. They have not put forward any experimental evidence in support of their empirical formula. It was therefore felt necessary to determine the limits

of suitability of the commonly present salts in the irrigation water. The object of this investigation is to study in detail the chemical behaviour of the various salines usually present in the irrigation waters, their ultimate effect upon the soil, and rendering the unsuitable waters fit for irrigation.

EXPERIMENTAL

(i). Experiments were carried out to study the nature of the reactions taking place during the use of water containing different salts for irrigation.

Seven circular plots of land of 16" diameter were enclosed by galvanised iron sheets up to a depth of 1'-3". About 4" of galvanised iron sheet were kept above the natural surface for the facility of irrigation. One inch irrigation at a time, with sodium carbonate solution of strengths varying from 10 parts to 60 parts per 100 litres, was given daily. The losses due to evaporation during the experiments were not determined. One plot was irrigated with tap water which contained 15 parts per 100,000 of salts and this served as a control. Soil samples were taken after 17 and 32 inches of irrigation. Initial and final p_H value, initial and final exchangeable calcium and sodium plus potassium were determined.

The methods used for these determinations were:—

1. p_H value by glass electrode (of 1 : 5 soil-water suspension).
2. Exchangeable calcium by Puri's method (Puri, *Soil Sci.*, 1935, **40**, 383).
3. Exchangeable sodium and potassium by Puri's method (Puri, *ibid.*, 1935, **40**, 249).
4. Degree of alkalisation (D. A.) i.e., the ratio of the amount of exchangeable monovalent bases (Na + K) in the soil to the maximum amount of monovalent ion the soil is capable of binding by exhaustive treatment with a neutral salt, the soils being alkaline; the latter has been taken to be equivalent to the sum of the major bases present in the exchange complex e.g. Na + K + Ca + Mg.

$$D. A. = \frac{Ex (Na + K)}{Ex (Na + K + Ca + Mg)} \times 100.$$

The results are given in Table I.

TABLE I

Effect of sodium carbonate solution on soil constants.

Serial No.	Salt conc.*	p_H			Degree of alkalisation			Total salts percentage		
		Initial.	After irrigation of 17".	After irrigation of 32".	Initial.	After irrigation of 17".	After irrigation of 32".	Initial.	After irrigation of 17".	After irrigation of 32".
1	0.00	8.28	8.25	8.45	8.7	8.2	10.4	0.10	0.10	0.11
2	10.0	8.00	8.18	8.42	8.1	13.3	14.2	0.12	0.11	0.12
3	20.0	7.85	8.38	8.60	5.6	13.4	20.0	0.08	0.10	0.11
4	30.0	8.50	8.75	9.40	10.1	20.3	25.5	0.11	0.12	0.12
5	40.0	8.31	8.70	9.10	2.8	21.5	20.9	0.06	0.08	0.10
6	50.0	7.85	8.80	8.90	5.5	30.6	35.5	0.08	0.09	0.08
7	60.0	8.27	8.85	9.20	5.2	23.7	27.3	0.08	0.12	0.13

* In parts per 100,000.

The results show that tap water has no effect on the p_H value or the degree of alkalisation of the soil, while in all the other cases there is a definite increase in the p_H value, which is more marked with high concentrations of sodium carbonate. There is an increase in the degree of alkalisation proportionate to the salt concentration.

The results further indicate that even if the irrigation water has sodium carbonate concentrations below 60 parts per 100 litres, deterioration of the soil might result. Hence irrigation waters, which might appear good for crop cultivation in the beginning for a certain soil and a particular crop, might have a lasting ill effect on the soil.

It was also observed that when the sodium carbonate solution was added to the plots, it took some time to disappear from the soil surface. The solution (20 c. c.) was pipetted out and titrated for carbonate and bicarbonate. The results are given in Table II. If the carbonate solution was not converted into bicarbonate, it would have considerably affected the p_H value and the exchangeable bases of the soil.

TABLE II
Conversion of Na_2CO_3 into NaHCO_3 .

Temp. = 23°

Na_2CO_3 conc. (parts per 100,000)	% Na_2CO_3 converted into NaHCO_3 1.5 hours.	2.0 hours.
10.0	50.0	50.0
20.0	37.5	35.0
30.0	41.5	41.7
40.0	25.0	31.3
50.0	20.0	25.0
60.0	20.8	29.2

(ii). In order to determine the effect of other salts in irrigation waters on the soil constants, a different procedure was adopted which is described below.

A typical Punjab soil (50 g.) was taken in a Buchner funnel and leached with solutions of increasing strengths of sodium chloride, sodium sulphate and sodium bicarbonate in 100 c.c. lots. After passing 4000 c.c. which is equivalent to (about 40 inches of irrigation) the soils were dried and examined for p_H and exchangeable bases. The results are given in Table III.

TABLE III
Effect of NaCl , Na_2SO_4 and NaHCO_3 solution on soil constants.

(a) Effect of NaCl .				(b) Effect of Na_2SO_4 .				(c) Effect of NaHCO_3 .		
Salt (parts per 100,000).	p_H .	Degree of alkalisation.	Total salts.	p_H .	Degree of alkalisation	Total salts.		Degree of alkalisation	Total salts.	
0.0	7.50	4.10	0.130%	7.50	4.10	0.13%	7.5	4.10	0.13%	
10.0	8.05	12.7	0.14	8.0	10.8	0.14	8.3	22.6	0.17	
20.0	8.15	13.7	0.14	7.9	11.5	0.14	8.55	28.7	0.21	
30.0	8.10	15.1	0.15	8.4	20.3	0.16	8.80	45.8	0.25	
40.0	8.10	16.7	0.15	8.3	17.6	0.15	9.35	69.5	0.27	
50.0	8.25	18.4	0.15	8.3	24.0	0.17	9.65	80.3	0.31	
60.0	8.30	19.2	0.15	8.5	26.5	0.17	9.88	84.0	0.35	

It will be seen that there is a gradual increase in the p_H value and in the degree of alkalisation, although the salt concentrations taken are all within the permissible limits of 60 parts per 100,000. These results clearly indicate that prolonged irrigation with such waters would produce slow deterioration of the soil, sodium bicarbonate being the most deleterious. There is a marked increase in the total salt content of soils treated with sodium-bicarbonate. Some of the sodium bicarbonate was left free in the soil, hence there was a marked increase in the total salts, and degree of alkalisation.

(iii). Experiments were next undertaken to determine the effect of irrigation waters having different salt indices on the soil. The same soil (25 g.) was taken in different Buchner funnels and leached with 2000 c.c. of water samples having different salt concentrations and salt indices. The p_H value, exchangeable calcium and exchangeable sodium plus potassium, before and after leaching, are given in Table IV.

TABLE IV

Effect of leaching on a typical Punjab soil with water samples of varying salt indices.

Sr. No	Salt index of waters.	Salts in parts per 100,000.	p_H .	Degree of alkalisation.	Total salt.
1	Original soil	...	8.50	11.40	0.13%
2	- 2.35	81.2	8.00	9.1	0.10
3	-35.94	28.3	8.00	10.9	0.11
4	-73.51	54.5	7.97	4.4	0.10
5	-93.48	73.0	7.85	6.6	0.11
6	+ 5.20	95.0	9.30	23.5	0.15
7	+23.68	128.0	9.33	40.8	0.17
8	+31.96		9.90	42.0	0.18
9	+37.40	161.2	9.85	58.3	0.18
10	+38.01	165.5	9.48	46.7	0.17
11	+390.17	1212.9	9.32	50.3	0.22

The p_H value remains almost the same with water samples of negative salt indices, but waters having positive salt indices increase the p_H value to such an extent that the soil attains the deterioration limits.

Moreover, there is a definite decrease in the degree of alkalisation with negative salt indices and its increase with positive salt indices. Hence, deterioration would be sure to result with waters having positive salt indices, while reclamation would be possible with waters of negative salt indices.

(iv). To study in greater detail the effect of water samples having positive salt indices, a special type of soil of high base exchange capacity (56 m.e.), high exchangeable calcium (54.1 m.e.) and high clay (58.9%) was used, as such a soil was expected to give a clearer indication of the effect of positive salt index on the exchangeable bases. The soil sample (25 g.) was leached in a Buchner funnel with 500 and 1000 c.c. of water in 100 c.c. lots. The results are given in Table V.

TABLE V

Effect of leaching with waters of positive salt indices of a black cotton soil.

Sr. No.	Salt index.	Total salts in parts per 100,000.	Vol. of leachate.	p_H .	Degree of alkalisation.	Total salts.
1	Original soil	8.00	4.1	0.06%
2	+ 22.70	130.7	500 c. c	8.57	5.7	0.08
3	+ 22.7	130.7	1000	8.8	5.0	0.10
4	+ 31.98	176.3	500	8.23	6.2	0.10
5	+ 31.98	176.3	1000	8.30	9.0	0.11
6	+379.72	1152.3	500	8.15	25.5	0.16
7	+379.72	1152.3	1000	8.60	28.2	0.17
8	+391.07	1188.8	500	8.42	23.4	0.19
9	+391.07	1188.8	1000	8.40	26.6	0.20

The results show an increase in the p_H value in all the cases and that in some cases the soil even reaches the limits of deterioration.

There is a regular increase in the degree of alkalisation showing the deteriorating effect of positive salt index.

Thus the results point towards the deterioration of soils with waters of positive salt indices.

(v). Taylor, Puri and Asghar (*loc. cit.*) stated that all waters having 60 to 120 parts of total solids per 100 litres and having negative salt indices were suitable for irrigation purposes.

To verify this statement, leaching was carried out with water samples containing total solids varying from 32 parts to 103 parts. The results are presented in Table VI.

TABLE VI

Effect of leaching with waters of varying salt indices having total salts less than 120.

Sr. No.	Salt index.	Total salts in parts per 100,000.	Vol. of leachate.	p_H	Degree of alkalisation.	Total salt.
1	Original soil	8.00	4.1	0.06%
2	-30.29	32.62	500 c.c.	8.25	...	0.07
3	-30.29	32.62	1000	8.30	...	0.07
4	-15.28	40.62	500	8.45	...	0.06
5	-15.28	40.62	1000	8.45	...	0.08
6	- 8.72	56.16	500	8.30	3.7	0.10
7	- 8.72	56.16	1000	8.35	5.5	0.08
8	-94.97	76.18	500	8.00	...	0.08
9	-94.97	76.18	1000	7.95	...	0.09
10	+ 0.36	84.13	500	8.42	4.2	0.10
11	+ 0.36	84.13	1000	8.52	4.3	0.11
12	+10.33	96.09	500	8.90	8.8	0.09
13	+10.33	96.09	1000	8.93	9.8	0.10
14	+11.91	103.26	500	8.50	9.9	0.11
15	+11.91	103.26	1000	8.80	9.7	0.10

This shows that, with negative salt indices, the degree of alkalisation reduces to zero, while with positive salt indices, although the total solids are within the permissible limits, there is a gradual increase in the degree of alkalisation.

Treatment of Waters Unsuitable for Irrigation

It is well known that waters unfit for irrigation can be improved by the addition of calcium salts. Four such samples of water were treated with calcium sulphate (5 g. to 1000 c. c.), the solution filtered to remove any excess of calcium sulphate and the filtrates analysed. The results of analysis before and after treatment are given in Table VII.

TABLE VII

Effect of calcium sulphate on the quality of water.

Water No →	1		2		3		4	
Salt contents.	After CaSO ₄		After CaSO ₄		After CaSO ₄		After CaSO ₄	
	Original.	treatment	Original	treatment	Original.	treatment.	Original.	treatment
Parts per 100 litres.								
CaSO ₄	..	118.32	..	87.7	..	48.28	...	120.36
Ca(HCO ₃) ₂ as CaCO ₃	20.00	41.50	23.75	53.00	16.00	59.00	6.50	39.00
CaCl ₂
Na ₂ SO ₄	40.00	24.85	35.00	63.35	20.00	71.10	40.00	87.53
Na ₂ CO ₃	12.72	..	20.14	..
NaHCO ₃ as Na ₂ CO ₃	24.38	...	31.54	...	38.16	...	25.44	...
NaCl	29.84	29.84	32.76	32.76	11.70	11.70	11.70	11.70
Total	114.22	214.51	123.05	226.81	98.58	190.18	103.78	258.59
p _H	8.85	7.75	7.95	7.40	8.20	7.18	8.55	7.40
Salt index	+10.76	-173.46	-13.39	-66.94	+8.65	-71.48	+12.83	-163.21

The decrease in p_H was well marked and the salt index changed from a positive to a large negative value, in all the cases showing that waters were rendered harmless.

Another substance which might be used for treatment of such waters is calcium permutite. Five hundred c. c. of water were treated with 5 g. of calcium permutite and kept for about 3 hours. These were filtered and the filtrate analysed. The results are given in Table VIII, and show a marked decrease in total solids.

TABLE VIII

Effect of calcium permutite on the quality of water

Sr. No.	Total salts in parts per 100,000.		Salt index	
	Original.	After treatment.	Original	After treatment.
1	103.16	89.10	+12.92	+1.50
2	124.41	82.38	+23.70	+2.97
3	123.76	87.91	+14.09	-60.99
4	90.23	58.04	+7.93	-24.16

The high positive index either changes to a negative one or decreases in magnitude. Calcium permutite is therefore another suitable substance for treatment of such waters.

PHYSICO-CHEMICAL STUDIES ON THE COMPOSITION OF COMPLEX
METALLIC FERRO AND FERRICYANIDES. PART IV.
THERMOMETRIC STUDY OF THE COMPOSITION
OF CADMIUM FERROCYANIDE

BY ABANI K. BHATTACHARYA AND HARISH C. GAUR

The composition of cadmium ferrocyanide has been studied by the thermometric method by the direct and the reverse methods in aqueous and in aqueous alcoholic media. The composition arrived at approximates to $K_2CdFeCy_6$, and is also affected by factors such as hydrolysis and adsorption.

Wyrouboff (*Ann. chim. phys.*, 1876, v, 8, 444) found that whatever be the proportion of cadmium salt relative to potassium ferrocyanide, the composition of the precipitate corresponded to $K_8Cd_8[(FeCy_6)]_4$. When precipitated in ammoniacal solution, the precipitate was found by Miller and Fisher (*J. Amer. Chem. Soc.*, 1900, 22, 537) to correspond to $K_2CdFeCy_6$, while in acid solution its composition was found by them to lie between this and the one proposed by Wyrouboff. This was confirmed by Mackay (*J. Chem. Soc.*, 1899, 75, 940) who stated that it required about 2.5% less potassium ferrocyanide to precipitate cadmium than would be required by $K_2CdFeCy_6$. Miller (*J. Amer. Chem. Soc.*, 1902, 24, 226) on the other hand found that $K_2CdFeCy_6$ was precipitated with K_4FeCy_6 in excess only from an alkaline or acid medium, whilst the one from neutral salt contained a larger proportion of Cd. With cadmium in excess, the composition of the precipitate in neutral solution was found to correspond with $K_8Cd_{10}(FeCy_6)_7$.

Treadwell and Chervat (*Helv. Chim. Acta*, 1922, 15, 633) found by electrometric titrations, that only in highly dilute solutions the precipitate approximated to the composition $K_2CdFeCy_6$. Kolthoff (*Z. anal. Chem.*, 1923, 62, 209) followed the method of conductometric titrations and concluded that at first the normal salt $K_2CdFeCy_6$ was precipitated, which, with further quantity of the reagent, gave the double salt $K_2Cd_3(FeCy_6)_2$.

In view of these conflicting opinions it was considered worthwhile to study the composition of this compound by thermometric, conductometric and potentiometric methods of analysis, with a view to arriving at a more definite conclusion. In this paper the results of thermometric titrations have been discussed.

EXPERIMENTAL

The arrangement for the thermometric titrations was similar to the one used by Halder (*J. Indian Chem. Soc.*, 1946, 23, 147). Reagents used were of 'Analar' (B. D. H.) quality. Cadmium sulphate solution was estimated by the electrolytic method. Potassium ferrocyanide solution was estimated by titrating against standardised potassium permanganate solution (Treadwell and Hall "Analytical Chemistry", Part II, p. 536).

Using different concentrations of the two salt solutions the titrations were followed by the direct and the reverse methods. The titrations were also made in the presence of alcohol up to a total concentration of 20% by volume.

$M/5.41$ solution of cadmium sulphate would be referred as $A/1$ solution of CdSO_4 and $M/4.99$ solution of potassium ferrocyanide as $A/1$ solution of K_4FeCy_6 .

Direct Thermometric Titrations

Cadmium sulphate from the burette was added to potassium ferrocyanide solution taken in the thermo-flask and mixed with varying amounts of alcohol.

TABLE I

$A/10\text{-K}_4\text{FeCy}_6 = 20 \text{ c.c.}$
Alcohol = nil.
(Fig. 1, curve 1).

$A/2\text{-CdSO}_4$ added.	Total rise in temp.
0.0 c.c.	0.000°
0.5	0.030
1.0	0.065
1.5	0.095
2.0	0.120
2.5	0.155
3.0	0.185
3.5	0.215
4.0	0.250
4.5	0.280
5.0	0.305
5.5	0.315
6.0	0.330
6.5	0.340
7.0	0.350
7.5	0.360
8.0	0.365

TABLE II

$A/10\text{-K}_4\text{FeCy}_6 = 18 \text{ c.c.}$
Alcohol = 2 c.c.
(Fig. 1, curve 2).

$A/2\text{-CdSO}_4$ added	Total rise in temp.
0.0 c.c.	0.000°
0.5	0.040
1.0	0.080
1.5	0.125
2.0	0.170
2.5	0.215
3.0	0.255
3.5	0.290
4.0	0.330
4.5	0.355
5.0	0.375
5.5	0.390
6.0	0.400
6.5	0.410
7.0	0.425
7.5	0.440

TABLE III

$A/10\text{-K}_4\text{FeCy}_6 = 16 \text{ c.c.}$
Alcohol = 4 c.c.
(Fig. 1, curve 3).

$A/2\text{-CdSO}_4$ added	Total rise in temp.
0.0 c.c.	0.000°
0.5	0.050
1.0	0.110
1.5	0.185
2.0	0.255
2.5	0.315
3.0	0.390
3.5	0.450
4.0	0.495
4.5	0.520
5.0	0.540
5.5	0.570
6.0	0.595
6.5	0.620

TABLE IV

$A/10\text{-K}_4\text{FeCy}_6 = 20 \text{ c.c.}$
Alcohol = nil.
(Fig. 2, curve 4).

$A/4\text{-CdSO}_4$ added.	Total rise in temp.
0.0 c.c.	0.000°
1.0	0.060
2.0	0.125
3.0	0.180
4.0	0.240
5.0	0.290
6.0	0.345
7.0	0.390
8.0	0.440
9.0	0.480
10.0	0.510
11.0	0.540
12.0	0.560
13.0	0.575
14.0	0.590
15.0	0.610

TABLE V

$A/10\text{-K}_4\text{FeCy}_6 = 18 \text{ c.c.}$
Alcohol = 2 c.c.
(Fig. 2, curve 5).

$A/4\text{-CdSO}_4$ added.	Total rise in temp.
0.0 c.c.	0.000°
1.0	0.055
2.0	0.110
3.0	0.165
4.0	0.210
5.0	0.265
6.0	0.320
7.0	0.360
8.0	0.395
9.0	0.420
10.0	0.445
11.0	0.465
12.0	0.485
13.0	0.500

TABLE VI

$A/10\text{-K}_4\text{FeCy}_6 = 16 \text{ c.c.}$
Alcohol = 4 c.c.
(Fig. 2, curve 6).

$A/4\text{-CdSO}_4$ added	Total rise in temp.
0.0 c.c.	0.000°
1.0	0.080
2.0	0.210
3.0	0.330
4.0	0.430
5.0	0.520
6.0	0.600
7.0	0.660
8.0	0.720
9.0	0.760
10.0	0.800
11.0	0.830
12.0	0.860
13.0	0.880

Reverse Thermometric Titrations

Potassium ferrocyanide from burette was added to cadmium sulphate in the thermo-flask, and mixed with varying amounts of alcohol.

TABLE VII

A/10-CdSO₄=20 c.c.
Alcohol=nil.
(Fig. 3, curve 7).

A/4-K ₄ FeCy ₆ added.	Total rise in temp.
0.0 c.c.	0.000°
0.5	0.005
1.0	0.020
1.5	0.040
2.0	0.060
2.5	0.075
3.0	0.100
3.5	0.120
4.0	0.145
4.5	0.165
5.0	0.185
5.5	0.205
6.0	0.230
6.5	0.255
7.0	0.265
7.5	0.275
8.0	0.280
8.5	0.295
9.0	0.305

TABLE VIII

A/10-CdSO₄=18 c.c.
Alcohol=2 c.c.
(Fig. 3, curve 8).

A/4-K ₄ FeCy ₆ added.	Total rise in temp.
0.0 c.c.	0.000°
0.5	0.030
1.0	0.050
1.5	0.080
2.0	0.110
2.5	0.140
3.0	0.175
3.5	0.200
4.0	0.230
4.5	0.255
5.0	0.285
5.5	0.315
6.0	0.335
6.5	0.350
7.0	0.360
7.5	0.370
8.0	0.385
8.5	0.400

TABLE IX

A/10-CdSO₄=16 c.c.
Alcohol=4 c.c.
(Fig. 3, curve 9).

A/4-K ₄ FeCy ₆ added.	Total rise in temp.
0.0 c.c.	0.000°
0.5	0.040
1.0	0.085
1.5	0.140
2.0	0.185
2.5	0.240
3.0	0.285
3.5	0.330
4.0	0.365
4.5	0.415
5.0	0.445
5.5	0.485
6.0	0.505
6.5	0.525
7.0	0.545
7.5	0.555
8.0	0.570
8.5	0.585

TABLE X

A/10-CdSO₄=20 c.c.
Alcohol=nil.
(Fig. 4, curve 10).

A/8-K ₄ FeCy ₆ added.	Total rise in temp.
0.0 c.c.	0.000°
2.0	0.000
3.0	0.005
4.0	0.015
5.0	0.030
6.0	0.045
7.0	0.065
8.0	0.085
9.0	0.105
10.0	0.125
11.0	0.145
12.0	0.165
13.0	0.185
14.0	0.205
15.0	0.215
16.0	0.225
17.0	0.235
18.0	0.245
19.0	0.255

TABLE XI

A/10-CdSO₄=18 c.c.
Alcohol=2 c.c.
(Fig. 4, curve 11).

A/6-K ₄ FeCy ₆ added.	Total rise in temp.
0.0 c.c.	0.000°
1.0	0.025
2.0	0.050
3.0	0.090
4.0	0.130
5.0	0.165
6.0	0.200
7.0	0.235
8.0	0.270
9.0	0.300
10.0	0.330
11.0	0.350
12.0	0.380
13.0	0.400
14.0	0.410
15.0	0.420
16.0	0.430
17.0	0.440
18.0	0.440
19.0	0.450

TABLE XII

A/10-CdSO₄=16 c.c.
Alcohol=4 c.c.
(Fig. 4, curve 12).

A/8-K ₄ FeCy ₆ added.	Total rise in temp.
0.0 c.c.	0.000°
1.0	0.090
2.0	0.180
3.0	0.265
4.0	0.340
5.0	0.405
6.0	0.465
7.0	0.520
8.0	0.575
9.0	0.620
10.0	0.660
11.0	0.695
12.0	0.725
13.0	0.750
14.0	0.775
15.0	0.785
16.0	0.800
17.0	0.810
18.0	0.825

DISCUSSION

Considering the strengths of the solutions of cadmium sulphate ($M/5.41$) and potassium ferrocyanide ($M/4.99$), theoretical titre values required for 20 c.c. of K_4FeCy_6 for the formation of the compounds $K_2CdFeCy_6$, Cd_2FeCy_6 and $K_2Cd_3(FeCy_6)_2$ in direct titrations would be 21.68, 43.36, and 32.52 c.c. respectively of cadmium sulphate solution. For the reverse titrations, theoretical titre values for the formation of the above compounds would be 18.44, 9.22 and 12.30 c.c. respectively of potassium ferrocyanide solution.

The observed titre value in aqueous medium in the case of direct titrations (23.0 c.c.) is slightly higher than the theoretical one required for the formation of $K_2CdFeCy_6$. In the reverse case the observed value (17.0 c.c.) in aqueous medium is lower than the theoretical one required for the formation of the same compound. The discrepancy between the observed and the theoretical titre values can be explained on the tendency of the compound formed to hydrolyse. Then potassium ferrocyanide, thus released,

FIG. 1

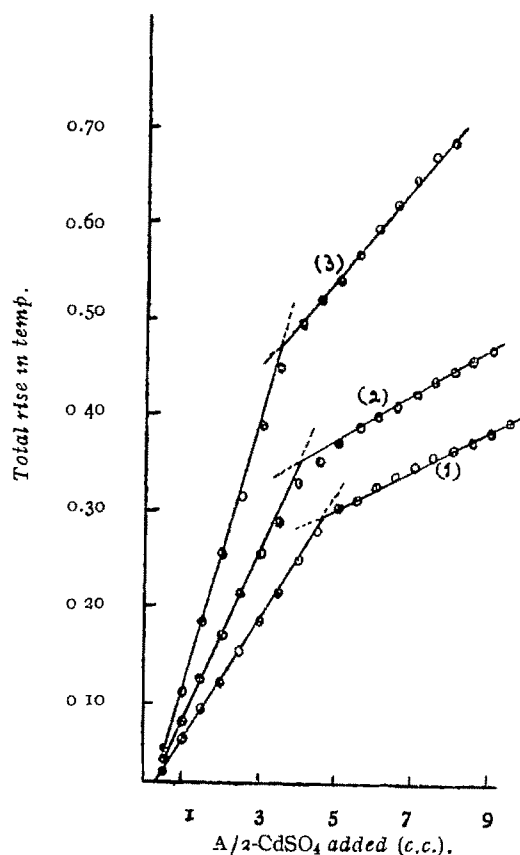


FIG. 2

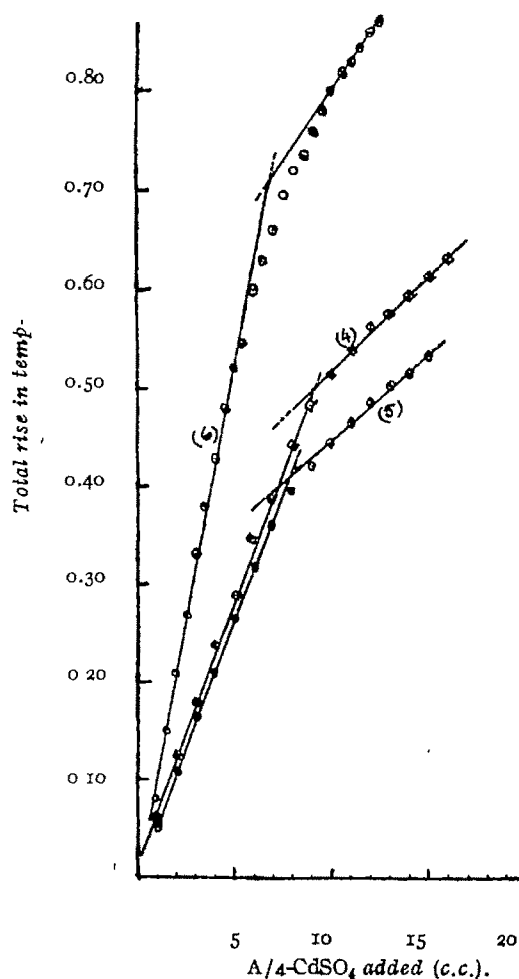


FIG. 3

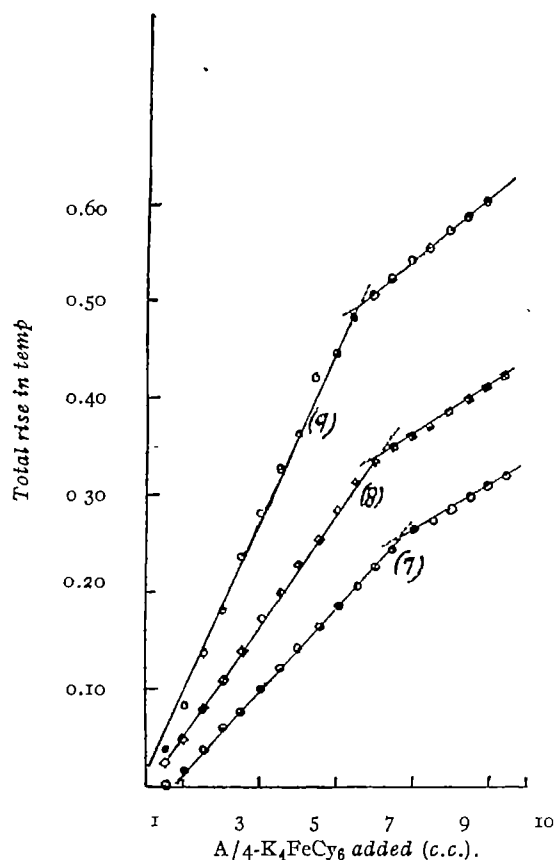
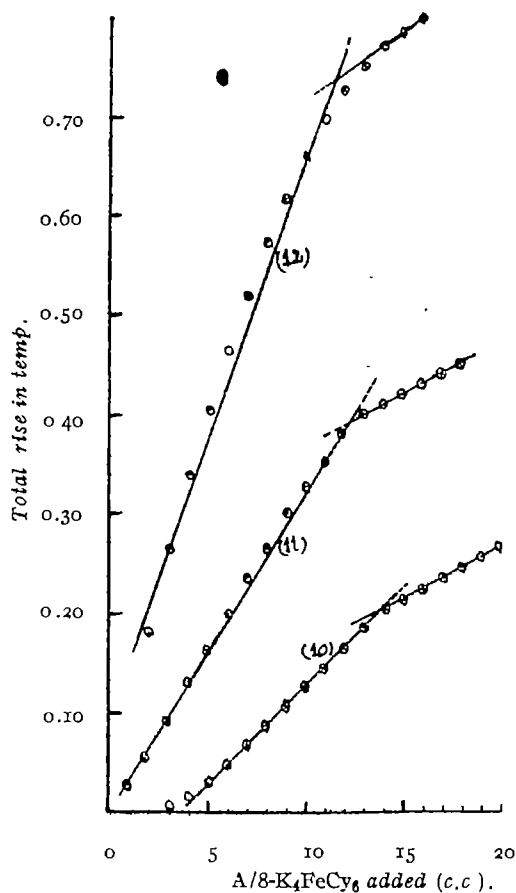


FIG. 4



would react with more of cadmium sulphate with the result that the titre values in aqueous solutions would be greater in the direct titrations and less in the reverse titrations.

The effect of addition of alcohol in increasing amounts in direct titrations is to gradually decrease the observed titre values; in the reverse titrations an increase is observed under the same conditions. This can be explained as being due to the check of hydrolysis of the compound. The observed titre values in the presence of increasing amounts of alcohol should thus correspond more closely to the theoretical values in the direct and the reverse titrations. This has been actually observed.

Similar reasoning has been advanced by us in the case of copper ferrocyanide (*cf.* Parts I-III, this *Journal*, 1947, **24**, 487, 499; 1948, **25**, 27).

The adsorption of cadmium and ferrocyanide ions by cadmium ferrocyanide sol has been observed. The adsorption of these ions, from the surrounding solution by the precipitate would be to decrease the titre value in aqueous medium in both the cases, which should then increase in the presence of alcohol. This is observed only in the reverse titrations, whereas there is a decrease in the titre value in the direct titrations in

presence of alcohol. This suggests that the effect of adsorption is masked, and the role of hydrolysis is more predominant during the precipitation of cadmium ferrocyanide. It appears that these facts were not taken into consideration by previous authors and this is the reason that so conflicting views have been expressed on the composition of cadmium ferrocyanide.¹

A break in the thermometric titration curve corresponding to the formation of $K_2Cd_3(FeCy_6)_2$, obtained in the conductometric study of the compound by Kolthoff (*loc. cit.*), has not been observed. The observation of Treadwell and Chervet (*loc. cit.*) that only in highly dilute solutions the precipitate approximate to the exact composition, $K_2CdFeCy_6$, does not seem to be reproducible, because in highly dilute solutions, the chances of the compound to hydrolyse would be still greater. The observation of Mackay (*loc. cit.*) that it requires about 2.5% less potassium ferrocyanide to precipitate the cadmium salt than would be required by $K_2CdFeCy_6$, supports the viewpoint of hydrolysis of the compound as observed by us.

Thermometric studies therefore support the formation of the compound $K_2CdFeCy_6$, but this is affected by factors like adsorption and hydrolysis.

Thanks are due to Dr. S. S. Deshapande for his kind interest in these investigations. One of the authors (H. C. G.) expresses his gratefulness to Principal K. C. Mehta of Agra College for the grant of a Research Fellowship.

CHEMICAL LABORATORY,
AGRA COLLEGE, AGRA.

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PHYSICO-CHEMICAL STUDIES ON THE COMPOSITION OF COMPLEX METALLIC FERRO AND FERRICYANIDES. PART V. POTENTIOMETRIC STUDY OF THE COMPOSITION OF CADMIUM FERROCYANIDE USING THE FERRO-FERRICYANIDE ELECTRODES

By ABANI K. BHATTACHARYA AND HARISH C. GAUR

The ferro-ferricyanide electrode has been employed in the potentiometric study of the composition of cadmium ferrocyanide. The results support the conclusions derived from the thermometric titrations in the formation of the compound $K_2CdFeCy_6$ and the influence of hydrolysis and adsorption in its precipitation (*cf* Part IV).

The oxidation potential of the ferro-ferricyanide electrode according to the equation,



is given by

$$E = E_0 + 0.059 \ln \frac{(FeCy_6)^{III}}{(FeCy_6)^{IV}} \quad (25^\circ).$$

As in the potentiometric study of copper ferrocyanide using the ferro-ferricyanide electrode (*J. Indian Chem. Soc.*, 1948, 26, 27) the titrating solution is potassium ferrocyanide containing 1% potassium ferricyanide with a platinised platinum electrode used in conjunction with a saturated calomel electrode. So long as there is an excess of cadmium ions in the solution, the concentration of ferrocyanide ions being small, the potential of the electrode is high. As soon as the cadmium ions are quantitatively precipitated, the next drop of ferrocyanide solution causes a sudden increase in $(FeCy_6)^{IV}$, and hence a sudden decrease in the oxidation potential occurs. This corresponds to the equivalence point.

EXPERIMENTAL

Standard solutions were prepared as described in part IV of this series (this issue, p. 185). The titrations were made using different concentrations of the titrant. $M/5.0$ solution of potassium ferrocyanide would be referred as A/1 solution of potassium ferrocyanide, and $M/5.41$ solution of cadmium sulphate as A/1 solution of $CdSO_4$.

TABLE I

A/10- $CdSO_4$ soln. = 20 c.c. (Fig. 1).

A/2- K_4FeCy_6 added.	$E_{obs.}$	A/2- K_4FeCy_6 added.	$E_{obs.}$	A/2- K_4FeCy_6 added.	$E_{obs.}$	A/2- K_4FeCy_6 added.	$E_{obs.}$
0.0 c.c.	0.4428 volt	1.9 c.c.	0.3166 volt	3.2 c.c.	0.3055 volt	4.0 c.c.	0.1212 volt
0.5	0.3340	2.0	0.3156	3.4	0.2995	4.1	0.1140
1.0	0.3278	2.2	0.3136	3.5	0.2905	4.2	0.1090
1.2	0.3268	2.4	0.3116	3.6	0.2885	4.3	0.1040
1.4	0.3227	2.6	0.3096	3.7	0.1854	4.4	0.0916
1.6	0.3207	2.8	0.3075	3.8	0.1466	4.5	0.0960
1.8	0.3176	3.0	0.3070	3.9	0.1318	4.6	0.0920

TABLE II

A/10-CdSO₄ soln. = 20 c.c. (Fig. 2).

A/4-K ₄ FeCy ₆ added.	E _{obs.}	A/4-K ₄ FeCy ₆ added.	E _{obs.}	A/4-K ₄ FeCy ₆ added.	E _{obs.}	A/4-K ₄ FeCy ₆ added.	E _{obs.}
0.0 c.c.	0.3410 volt	2.8 c.c.	0.3248 volt	5.6 c.c.	0.3075 volt	7.6 c.c.	0.1303 volt
0.4	0.3448	3.2	0.3223	6.0	0.3025	7.8	0.1190
0.8	0.3348	3.6	0.3200	6.4	0.3000	8.0	0.1130
1.2	0.3332	4.0	0.3176	6.8	0.2970	8.2	0.1040
1.6	0.3312	4.4	0.3155	7.0	0.3050	8.4	0.1000
2.0	0.3292	4.8	0.3125	7.2	0.2260	8.6	0.0970
2.4	0.3263	5.2	0.3104	7.4	0.1527		

TABLE III

A/10-CdSO₄ = 20 c.c. (Fig. 3),

A/8-K ₄ FeCy ₆ added.	E _{obs.}	A/8-K ₄ FeCy ₆ added.	E _{obs.}	A/8-K ₄ FeCy ₆ added.	E _{obs.}	A/8-K ₄ FeCy ₆ added.	E _{obs.}
0.0 c.c.	0.3512 volt	6.0 c.c.	0.3181 volt	11.5 c.c.	0.2870 volt	15.0 c.c.	0.2890 volt
1.0	0.3471	7.0	0.3054	12.0	0.2820	15.5	0.2015
2.0	0.3360	8.0	0.3003	12.5	0.2180	16.0	0.1476
3.0	0.3354	9.0	0.2910	13.0	0.2740	16.5	0.1293
4.0	0.3027	10.0	0.2870	13.5	0.2688	17.0	0.1171
5.0	0.3175	11.0	0.2932	14.0	0.2748	18.0	0.1070
							0.0880

TABLE IV

Results of the potentiometric titrations.

K ₄ FeCy ₆ .	CdSO ₄	Observed titre value for 20 c.c. of A/10 soln.	Equiv. vol. of A/10- K ₄ FeCy ₆ .	Curve No.
A/2	A/10	3.68 c.c.	18.4 c.c.	1
A/4	A/10	7.24	18.1	2
A/8	A/10	14.40	18.0	3

DISCUSSION

Considering the strengths of the solutions of potassium ferrocyanide (*M*/5.0) and cadmium sulphate (*M*/5.41) the theoretical titre value for 20 c.c. of cadmium sulphate solution for the formation of the compound K₂CdFeCy₆ is 18.5 c.c. of potassium ferrocyanide solution. Compounds Cd₂FeCy₆ and K₂Cd₃(FeCy₆)₂ require respectively 9.25 and 12.32 c.c. of potassium ferrocyanide solution.

FIG. 1

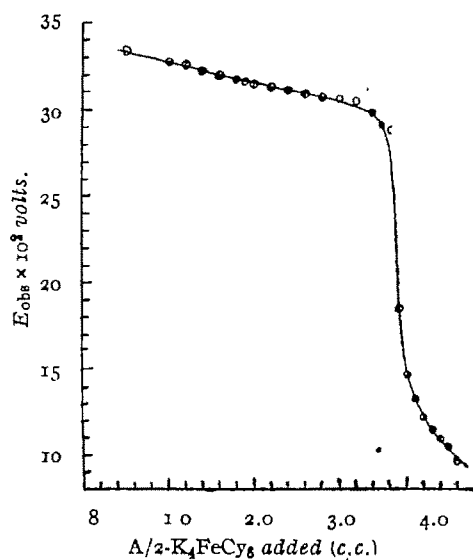


FIG. 2

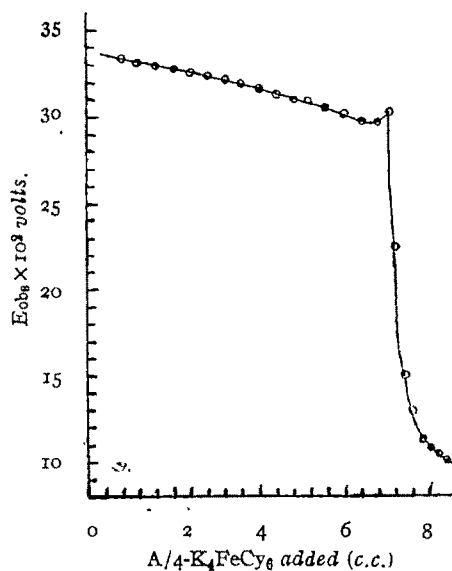
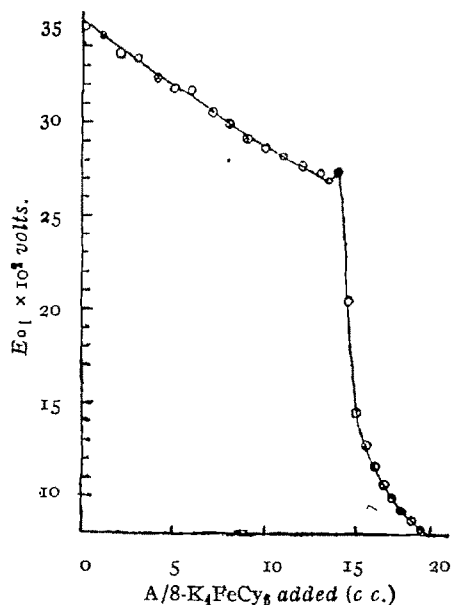


FIG. 3



The observed titre value is slightly lower than the theoretical one required for the formation of the compound $K_3CdFeCy_6$. This discrepancy between the observed and the theoretical titre value can be explained, as has been previously done (Part IV, *loc. cit.*) by considering the hydrolysable character of this compound and the influence of adsorption on its precipitation. Potassium ferrocyanide, released as a result of hydrolysis of the compound, would react with some cadmium sulphate, resulting in a

lowering of the observed titre value than the theoretical one. The adsorption of Cd^{++} ions by the precipitate would also tend to lower the observed titre values. A decrease in titre value with the increase of dilution is observed. This clearly shows that the extent of hydrolysis increases with the dilution.

As in the case of copper ferrocyanide, potentiometric titrations could not be carried in the presence of alcohol (which had been possible in the thermometric studies of the compound in Part IV of this series), because constant values of potential could not then be obtained.

Potentiometric studies support the thermometric conclusions regarding the formation of the compound $\text{K}_2\text{CdFeCy}_6$ and the important role of hydrolysis and adsorption in its precipitation.

The conductometric studies on the composition of the compound are in progress, and will be communicated shortly.

Thanks are due to Dr. S. S. Deshapande for the continued interest in the problem and to Dr. K. C. Mehta, Principal, Agra College, for having granted a research fellowship to one of us (H. C. G.).

CHEMICAL LABORATORIES,
AGRA COLLEGE, AGRA.

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REVIEWS

Colorimetric Determination of Traces of Metals—By E. B. Sandell. Published by Interscience Publishers Inc., New York. Pp. 487 + xvii. Price \$ 7.00.

It has been a common notion that the quantitative estimation of metals present in quantities less than 0.01% is only possible by spectro-chemical method. But this book has shown that colorimetric method can equally compete with the spectro-chemical method. It presents the rapid growth of colorimetric method in the last 20 years and is found to be a very valuable guide-book to analytical chemists dealing with quantitative estimation of micro quantity of metals. The discussions on trace-analysis and its general method at the beginning are very useful. It is interesting to note that one may improve the sensitivity of the measurement ten times by the use of spectrophotometer. But it has not been stressed that the precision of instruments is limited by their optical quality, by reflection and other mechanical consideration. The book contains many standard curves, useful tables and lists of commonly used colorimetric reagents which are very helpful to any chemist dealing with trace-analysis. The dithizone method has been treated very thoroughly and is found to be useful. Moreover, the book has treated the methods for individual metals in detail and may be recommended for trace-metal estimation everywhere. In the book, the author has shown his rich experience and knowledge in selecting proper methods and has also stressed that our knowledge of the application of colour reactions is still so imperfect that much work has yet to be done. The book has been found to be so useful that the users of it look forward to a similar treatment of remaining metals and non-metals in near future.

P. B. S.

Official and Tentative Methods of Analysis—Published by the Association of Official Agricultural Chemists, Sixth Edition, 1945. Pp. 932 + xii. Price \$ 6.75.

The compilation "A.O.A.C.—Methods of Analysis" is already well known to chemists who will, we feel sure, welcome publication of this new edition. There have been considerable additions and alterations in almost all the chapters in this edition and four new chapters have been added. Of the 894 pages comprising 44 chapters, only a few deal directly with agricultural problems; the rest are devoted to a variety of other topics which have been selected in such a way as to cover a very wide field of chemical analyses e.g. foods, drugs, etc. We recommend this book to all our readers interested in general analytical chemistry.

N. C. S.

STUDIES OF THE INFLUENCE OF 'AGEING' UNDER AN OZONISER DISCHARGE ON THE JOSHI EFFECT IN HIGH PRESSURE CHLORINE

By P. MALLIKARJUNAPPA

Influence of 'ageing' on the Joshi effect in high pressure chlorine has been studied. In a freshly prepared ozoniser, the effect varied appreciably with the time of exposure to discharge. This has been attributed, in part, to an interaction between the (electrode) wall material and the activated gas under the discharge, leading to the formation of a boundary layer on the electrodes. The influence of light frequency was investigated on the Joshi effect, produced at potentials 1 to 4 kV, and also in respect of its variation under 'ageing'. It was found that the effect Δi and % Δi varied *frequencywise*, viz., white > blue > green > red. The effect under unfiltered white was found to be less than the additive effect due to the filtered components, viz., blue, green and red; this difference decreased with the exciting potential. The influence of 'ageing' leading to the enhancement of the effect, Δi , followed the order: red > green > blue > white. Both the net and the relative effect increase with temperature in high pressure chlorine. Under constant mass conditions the rise of temperature brings about a rise in the gas pressure, which makes for an increase in Δi . An enhanced (due to heating) chemical action between the excited gas and the wall material also favours Δi , by abstracting from the extra high gas pressure, which ordinarily inhibits the effect Δi .

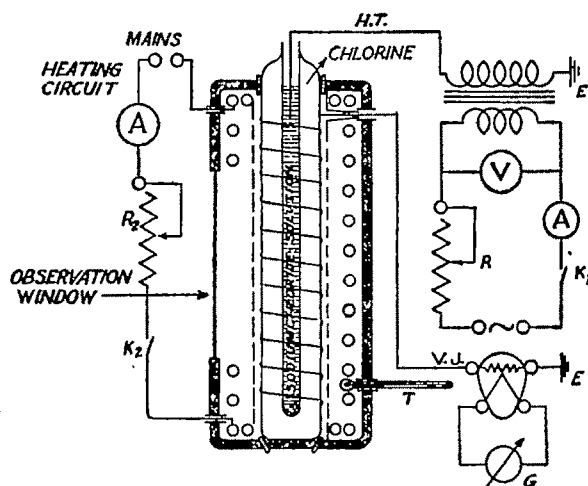
The marked dependence of the magnitude of the above phenomenon, Δi , an instantaneous and reversible photo-diminution of the discharge current, i , on factors such as the gas pressure, temperature, the net surface exposed to discharge, etc., is known (Joshi, *Proc. Indian Sci. Cong.*, 1943, Part II, Sec. III, p. 51). This effect, Δi , tends to increase with pressure up to a limit (about 93 % with but ordinary light at about 460 mm. pressure) and decrease thereafter (Joshi and Deo, *Nature*, 1944, **154**, 343). It was also found over a wide range of conditions that the Joshi effect decreased with temperature (Deo and Padmanabhulu, *Proc. Indian Sci. Cong.*, 1944, Part III, *Chem. Sec.*, *Abst.* No. 36; Deo and Urs, *ibid.*, 1945, *Phys. Sec.*, *Abst.* No. 16). A limitation of this deduction has now been observed in the use of gas pressure, much larger than those employed by earlier workers. The marked influence of ageing under discharge, on the magnitude and even sign of the above phenomenon, was observed by Joshi (*loc. cit.*), and is implicit in Joshi's recent theory thereof (*Proc. Indian Sci. Cong.*, 1946, Part III, *Phys. Sec.*, *Abst.* No. 26; *Curr. Sci.*, 1947, **16**, 19). This 'ageing' factor has now been investigated in some detail.

EXPERIMENTAL

The arrangement of the apparatus and the electrical circuit are shown in Fig. 1. Alternating potentials of 500 cycles frequency, obtained from a rotary converter and stepped up with a transformer, were applied to a Siemens' glass ozoniser containing chlorine, purified over liquid air, at 540 mm. pressure. The exciting potential was varied from 1 to 4 kV. In each series, the discharge current was observed in dark (i_d), and under irradiation (i_e) from a 220 volt, 200 watt incandescent (glass) bulb; a low

resistance Cambridge vacuo-junction along with a galvanometer was employed as a current detector. The values of i_D and i_L are given in arbitrary units of the galvanometer scale deflections. The system was enclosed in an electrical heater in the form of a rectangular box with asbestos walls, whose temperature could be varied in the range of 25° to 80° by regulation of the heating current. Two series of experiments were carried out, one with ozoniser A, and the other with ozoniser B, filled with purified chlorine at 540 mm. pressure.

FIG. 1



The variation of Joshi effect with 'ageing' under discharge in a fresh ozoniser A, at 2.67 kV (25°) was studied, and the results are given in Table I. Table II shows the influence of exciting potential (kV) and light frequency on Joshi effect in ozoniser A, 'aged' under discharge. The influence of light frequency on Joshi effect during ageing of the further aged ozoniser A, was also investigated and the results are tabulated in Table III. The comparative influence of temperature and exciting potential (kV) on the Joshi effect in a long aged ozoniser A, and fresh one B, was studied and the results are recorded in Table IV. The effective frequency of irradiation was varied by the use of appropriate light filters.

TABLE I

Variation of the Joshi-effect with ageing under discharge in a fresh ozoniser A, at 2.67 kV (25°).

Time.	i_D	i_L	Δi	% Δi	Time.	i_D	i_L	Δi	% Δi
0 min.	11.4	7.1	4.3	37.7	195 min.	13.4	7.7	5.7	42.5
15	11.4	7.1	4.3	37.7	210	13.4	7.7	5.7	42.5
30	13.0	8.7	4.3	33.1	225	13.4	7.7	5.7	42.5
45	14.0	8.9	5.1	36.4	240	13.6	7.7	5.9	43.1
60	12.6	7.7	4.9	38.9	255	13.8	7.7	6.1	44.2
75	12.8	7.4	5.4	42.2	270	13.8	7.7	6.1	44.2
90	12.6	7.4	5.2	42.3	285	13.8	7.7	6.1	44.2
105	13.0	7.7	5.3	40.8	300	14.1	8.1	6.0	43.5
120	13.0	7.7	5.3	40.8	315	16.1	9.7	6.4	40.0
135	13.0	7.4	5.6	43.1	330	16.1	9.7	6.4	40.0
150	12.8	7.4	5.4	42.2	345	16.1	9.7	6.4	40.0
165	13.4	7.7	5.7	42.5	360	16.1	9.7	6.4	40.0
180	13.4	7.7	5.7	42.5					

TABLE II

Influence of exciting potential (kV) and light frequency on the Joshi-effect in ozoniser A, 'aged' under discharge.

kV.		White (7800-3700Å)	Blue (4750-4000Å)	Green (5775-5070Å)	Red (7070-6070Å)
1.34	t_D	—	2.2	2.2	2.2
	t_L	—	2.2	2.2	2.2
	t_D	5.0	5.0	5.5	5.5
	t_L	1.6	2.5	3.3	4.4
1.6	Δi	3.4	2.5	2.2	1.1
	$\% \Delta i$	67.0	50.0	40.0	20.0
	i_D	8.0	8.1	8.7	8.1
	i_L	2.3	3.6	4.5	6.3
1.87	Δi	5.7	4.5	4.2	1.8
	$\% \Delta i$	71.0	55.0	48.0	22.2
	t_D	10.8	10.9	11.4	11.6
	t_L	3.0	4.5	5.9	8.9
2.14	Δi	7.8	6.4	5.5	2.7
	$\% \Delta i$	72.8	58.7	48.2	23.0
	i_D	12.8	13.2	14.7	14.5
	i_L	4.9	5.5	8.7	11.8
2.4	Δi	8.1	7.7	6.0	2.7
	$\% \Delta i$	62.8	58.3	40.8	18.6
	t_D	16.1	16.7	18.3	18.2
	t_L	6.3	8.1	11.6	15.3
2.67	Δi	9.8	8.6	6.7	2.9
	$\% \Delta i$	60.9	51.5	36.8	15.8
	t_D	20.2	21.2	23.9	23.9
	t_L	10.2	11.4	16.9	21.2
2.94	Δi	10.0	9.8	7.0	2.7
	$\% \Delta i$	49.4	46.2	29.2	11.3
	t_D	25.6	26.5	29.6	29.7
	t_L	15.5	16.6	22.9	27.4
3.21	Δi	10.1	9.9	6.7	2.3
	$\% \Delta i$	39.3	37.4	20.6	7.9
	t_D	31.2	31.6	35.6	34.8
	t_L	21.1	21.6	29.0	32.6
3.47	Δi	10.1	10.0	6.6	2.2
	$\% \Delta i$	32.3	31.6	18.5	6.3
	i_D	37.5	37.9	40.3	41.5
	i_L	27.0	27.4	33.7	39.2
3.74	Δi	10.5	10.5	6.6	2.3
	$\% \Delta i$	28.0	27.7	16.3	5.5
	t_D	45.0	45.2	47.2	47.9
	t_L	33.2	33.6	40.4	45.7
4.01	Δi	11.8	11.6	6.8	2.2
	$\% \Delta i$	26.0	25.6	14.4	4.5

TABLE III

*Influence of light frequency on the Joshi effect during ageing
of a further 'aged' ozoniser A.*

Time.	i_D	i_W	i_B	i_G	i_R	Δi_W	Δi_B	Δi_G	Δi_R	% Δi_W	% Δi_B	% Δi_G	% Δi_R
0 min.	32.2	27.2	29.8	29.8	30.2	5.0	2.4	2.4	1.0	15.5	7.4	7.4	3.1
15	29.1	24.3	25.3	25.7	27.7	4.8	3.8	3.4	1.4	16.5	13.0	11.4	4.8
30	30.0	25.0	27.7	27.9	29.5	5.0	2.3	2.1	0.5	16.7	7.6	7.0	1.6
45	31.3	26.1	28.5	28.8	30.0	5.2	2.8	2.5	1.3	16.6	8.9	8.0	4.1
60	35.7	28.5	30.7	31.5	32.7	7.2	5.0	4.2	3.0	20.1	14.0	11.7	8.4
75	34.5	27.9	30.7	31.0	32.1	6.6	3.8	3.5	2.4	19.1	11.0	10.1	7.0
90	37.3	31.1	33.3	33.8	36.5	6.2	4.0	3.5	0.8	16.9	10.7	9.4	2.1
105	37.1	29.1	30.5	31.0	34.9	8.0	6.6	6.1	2.2	21.5	18.0	16.4	6.0
120	41.8	33.3	33.8	34.5	38.5	8.5	8.0	7.3	3.3	20.3	19.1	17.4	7.9
135	41.9	34.4	37.1	37.9	39.9	7.5	4.8	4.0	2.0	17.9	11.4	9.5	4.7
150	41.0	34.1	35.1	37.1	39.4	6.9	4.9	3.9	1.6	16.9	11.9	9.3	3.9
165	42.5	35.6	37.9	38.3	40.6	6.9	4.6	4.2	1.9	16.2	10.8	9.8	4.2
180	41.6	34.9	37.3	38.5	38.9	6.7	4.3	3.1	2.7	16.1	10.3	9.4	6.4
195	43.1	35.2	38.5	38.7	39.4	7.9	4.6	4.4	3.7	18.3	10.7	10.2	8.5
210	40.9	32.7	34.9	35.4	37.4	8.2	6.0	5.5	3.5	20.0	14.6	13.4	8.5
225	42.7	34.8	36.6	37.8	38.5	7.9	6.1	4.9	4.2	18.5	14.3	11.4	9.8
240	42.2	35.1	35.9	36.5	37.8	7.1	6.3	5.7	4.4	16.8	14.9	13.5	10.4
255	41.3	34.5	36.6	38.5	38.5	6.8	4.7	2.8	2.8	16.4	11.9	6.6	6.6
270	42.2	34.8	37.0	37.9	40.1	7.4	5.3	4.3	2.1	17.5	12.3	10.1	5.0
285	41.0	33.8	36.1	36.9	37.6	7.2	4.9	4.1	3.4	17.5	11.9	10.0	8.2
300	41.3	34.9	36.6	37.1	37.7	6.4	4.7	4.2	3.6	15.4	11.3	10.1	8.7
315	39.9	33.9	35.4	36.9	37.0	6.9	4.5	3.0	2.9	17.2	11.2	7.5	7.2
330	41.0	33.8	36.1	36.9	37.6	7.2	4.9	4.1	3.4	17.5	11.9	10.0	8.7
345	41.0	33.8	36.1	36.9	37.6	7.2	4.9	4.1	3.4	17.5	11.9	10.0	8.7
360	41.0	33.8	36.1	36.9	37.6	7.2	4.9	4.1	3.4	17.5	11.9	10.0	8.7
375	41.0	33.8	36.1	36.9	37.6	7.2	4.9	4.1	3.4	17.5	11.9	10.0	8.7

TABLE IV

Comparative influence of temperature and exciting potential (kV) on the Joshi effect in a long 'aged' ozoniser A, and fresh one, B

kV.	Ozoniser A.								Ozoniser B.			
	25°	30°	35°	40°	45°	65°	70°	80°	25°	50°	60°	65°
1.34	i_D	—	—	—	—	11.8	12.0	12.6	10.9	—	—	—
	i_L	—	—	—	—	10.2	10.1	10.5	10.7	—	—	—
	Δi	—	—	—	—	1.6	1.9	2.1	0.2	—	—	—
	% Δi	—	—	—	—	13.5	16.0	16.6	1.8	—	—	—
1.60	i_D	14.8	16.0	16.2	16.6	17.2	19.2	23.0	23.7	16.4	20.7	23.2
	i_L	13.4	14.4	14.3	14.5	14.6	14.0	15.2	15.5	14.7	16.6	15.2
	Δi	1.4	1.6	1.9	2.1	2.6	5.2	7.8	8.2	1.7	4.1	6.6
	% Δi	9.4	10.0	11.6	12.6	15.1	27.0	33.6	34.6	10.3	19.8	28.4
1.87	i_D	21.0	22.4	22.9	23.7	25.7	29.1	34.5	37.7	23.9	34.8	37.0
	i_L	17.9	19.0	19.2	19.5	20.5	19.4	22.1	22.0	19.9	25.9	24.3
	Δi	3.1	3.4	3.7	4.2	4.9	9.7	12.4	15.7	4.0	8.9	12.7
	% Δi	14.9	15.1	16.1	17.7	19.2	33.3	35.9	41.6	16.7	25.5	34.3
2.14	i_D	26.4	30.9	31.8	31.8	34.3	39.4	46.6	51.1	31.3	47.7	51.0
	i_L	21.9	25.2	25.9	25.5	27.0	25.8	30.2	30.5	25.3	37.4	37.0
	Δi	4.5	5.7	5.9	6.3	7.3	13.6	16.4	20.6	6.0	10.3	14.0
	% Δi	17.0	18.4	18.5	19.8	21.2	34.5	35.2	40.3	19.1	21.5	27.4
2.40	i_D	37.4	41.9	39.1	40.1	43.1	50.5	59.4	66.4	40.6	60.4	64.1
	i_L	30.3	33.8	31.6	31.6	33.8	33.5	39.5	42.7	32.1	49.8	50.3
	Δi	7.1	8.1	7.5	8.5	9.3	17.0	19.0	23.7	8.5	10.6	13.8
	% Δi	19.0	19.3	19.1	21.2	21.5	33.6	33.5	35.6	20.9	17.5	21.5
2.67	i_D	48.1	52.5	49.8	52.4	54.9	62.8	74.6	83.1	49.1	71.2	80.3
	i_L	38.5	42.5	40.0	41.9	44.0	41.9	52.2	56.2	38.7	60.0	64.5
	Δi	9.6	10.0	9.8	10.5	10.9	20.9	22.4	26.9	10.4	11.2	15.5
	% Δi	19.9	19.0	19.6	20.0	19.8	33.2	30.0	32.3	21.1	15.7	19.6
2.94	i_D	61.6	65.7	62.1	65.4	68.6	79.3	—	—	63.6	—	—
	i_L	50.8	54.6	50.9	53.5	56.7	55.0	—	—	51.7	—	—
	Δi	10.8	11.1	11.2	11.9	11.9	24.3	—	—	11.9	—	—
	% Δi	17.0	17.5	18.0	18.1	17.3	30.6	—	—	18.7	—	—

DISCUSSION

The foregoing results given in Tables I-IV show that the Joshi effect corresponding to a photo-diminution of current in the range 2 to 73 % occurs in high pressure chlorine as used in the present work ; the effect increases in the order : red < green < blue < unfiltered white. This order is to be expected from general photochemical considerations. The results also show that the relative effect, viz.,

$$\frac{100 \times \Delta i}{i_D} = \% \Delta i,$$

where i_D is the current in dark, increases by increasing the applied potential (kV), and

reaches a maximum near 2.1 kV. The 'threshold potential' (Joshi, *Proc. Ind. Acad. Sci.*, 1945, **22 A**, 225) characterised by a sudden increase of i at V , and termed V_m , and near which the system breaks down as a dielectric, lay near 1.6 kV and was affected by temperature and what is more, by 'ageing' under discharge (*vide infra*). These results support Joshi's discrimination of 'threshold potential' from the Paschen or spark potential (*Curr Sci.*, 1939, **8**, 548 ; 1946, **15**, 281, 282).

The results in Table I, with ozoniser A, show that the current, i_b , at 2.7 kV tends to increase by nearly 40% after about 6 hours of ageing ; any additional exposure produces but a small increase in i_b . The above remark applies also to the current under light, i_L . It is interesting that both the net Joshi effect, $\Delta i = i_b - i_L$, and the relative effect, $\% \Delta i$, reach maximum at the above stage, and remain practically stationary thereafter. The above deduction holds for irradiations in various filtered bands as also the unfiltered white. The time variation in conductivity under fairly constant electrical conditions is attributable to a progress of chemical reaction between the excited gas and the walls of the ozoniser. Due to continued discharge as under 'ageing', a rise of temperature of about 15° to 25° occurred in the system. This should favour an increased chemical action, as also the circumstances that the gas pressure now used is much greater than that employed by previous workers in this line, a deduction in accord with Joshi's finding that the law of mass action may be applied to an appreciable extent to the chemical action produced under an electrical discharge (*Curr. Sci.*, 1945, **14**, 175).

Table II records the results of the influence of light frequency (mean) on the effect, Δi . The current in dark, i_b and under irradiation, i_L , in the various wave bands used, increase progressively with the applied potential. The variation of i_L in the different frequency regions at a given applied potential is in the order : red > green > blue > unfiltered white, and hence Δi , i.e., ($i_b - i_L$) varies in the opposite sense in respect of the frequency of light. It is interesting to note that the difference in respect of i_L in white and in blue light decreases with the exciting potential (kV), whereas the difference between blue and green or green and red increases with the exciting potential. Thus, e.g., the differences in the values of i_L between white and blue, blue and green, and green and red, are 1.8, 3.5 and 3.7 respectively at applied potential 2.67 kV, and 0.4, 7.4 and 6.4 respectively at 3.47 kV. It was also observed that the effect, Δi , under white (unfiltered) light was less than the additive effect due to the filtered components, viz., blue, green, and red. This difference in respect of $\% \Delta i$ decreases with increase of the exciting potential ; thus e.g., it decreases from 57.1 to 18.5 when the corresponding applied potential is increased from 2.14 to 4.01 kV. It follows from the above results that the light frequency is the main factor in the production of the above phenomenon. It is, however, interesting to see that the effect under white and blue is much more pronounced than that due to green and red. This may be associated with the circumstance that both the former regions include appreciably the main absorption band of chlorine, viz., 2300-5000 Å (Joshi, *loc. cit.*).

It may be mentioned here that when the experiments referred to above were completed, the ozoniser A had been exposed to the discharge for a period of 30 hours. The Joshi effect, Δi , was then observed in the various light bands, during a further continuous 'ageing', i.e., exposure to discharge for about 6 hours (*vide Table III*).

These results show that the current in dark, i_d , and the current under irradiation by white (unfiltered) light (i_w), blue light (i_b), green light (i_g), and red light (i_r), increase with time. The current i_d rises to a maximum in about 2 hours after which time it remains practically constant. Thus at the end of 2, 4 and 6 hours, the increase in i_d is 30%, 31% and 27% respectively. This remark also applies to the current under light in the above mentioned regions. The effect, Δi_{White} , Δi_{Blue} , Δi_{Green} , Δi_{Red} increases with time of exposure up to about 5 hours and remains practically constant thereafter. It is, however, interesting to note that this influence of ageing leading to the enhancement of the effect Δi , follows the order: red > green > blue > white. Thus, e.g., the increase of Δi_{White} at the end of 2, 4 and 6 hours is 70%, 42% and 44% respectively, whereas the corresponding increase of Δi_{Red} is 230%, 340% and 240% respectively.

An examination of the data in Table IV shows that i_d , i_r , and Δi increase progressively with the exciting potential (kV). With increase of temperature the 'threshold potential', V_m , however, decreases, e.g., V_m changes from 1.6 to 1.3 kV when the corresponding temperature is raised from 25° to 65°. At constant exciting potential (kV), i_d , Δi and $\% \Delta i$ increase with temperature. Thus, e.g., at 2.14 kV, i_d in dark increases from 26.4 at 25° to 51.1 at 80°. The net effect Δi and $\% \Delta i$ are respectively 4.5 and 17 at 25° and 19 and 38.1 at 80°. When the ozoniser was cooled from 80° to 25°, the effect Δi and $\% \Delta i$ were found to have undergone a *permanent* increase, compared with the corresponding values at this temperature, observed before heating the system. This deduction is borne out by the results in Table IV for the second ozoniser B, also filled with high pressure chlorine. This ozoniser B was, however, fresh, i.e., 'unaged' under discharge.

Joshi has emphasised the significance of the 'threshold potential' V_m , for discharge reactions in general and the effect Δi in particular (*Trans. Faraday Soc.*, 1929, **26**, 120; *Nature*, 1945, **164**, 147). He has shown that the current i depends upon $V - V_m$ (*Proc. Ind. Acad. Sci.*, 1945, **22A**, 389), and that Δi tends to increase with i over a certain limit. From the results in Table IV it is seen that $V - V_m$ increases, since V_m diminishes with temperature (*vide supra*), and hence the current i_d and the effect Δi increase. The change in Δi may also be attributed to the change in the wall surface at higher temperature. Chlorine is a reactive gas and much more so under electrical fields. Aided by high temperature and electric fields chlorine should react chemically with the wall material. These results in Table IV, showing an increase of Δi with temperature, are at variance with those of Deo and co-workers (*loc. cit.*), observed with much smaller gas pressure, viz., 148 mm. In Joshi's theory for the effect Δi , an electrode or a boundary layer, derived in part from the adsorption of ions and molecules of the excited gas, plays an important part. The extent of such interaction of the gas should be less at low gas pressure than at the large ones now used. It has been shown by Joshi that within limits, the pressure of the gas is a chief determinant of the magnitude of the effect. When the initial pressure of the gas under discharge is high, and when the system is heated, the pressure of the gas under discharge is high, and when the system is heated, the pressure will increase favouring an increase in Δi , and the further increase of pressure, which would ordinarily be inhibitory towards the effect, is removed by wall action leading to the formation of an adsorption layer of NaCl.

Under the conditions of the present experiment, there are two opposite tendencies at the higher temperature, one to decrease the effect due to the deranging of the boundary layer, and the other to increase the effect due to chemical action by some partial reduction of the extra gas pressure as mentioned above. The effect due to the enhanced interaction of the excited gas with the glass walls of the ozoniser would appear to be greater than that of (partial) destruction of the electrode layer due to heating. This view is in accord with the significant observation, mentioned above, viz, the effect at a given temperature is comparatively large when the gas is aged at higher temperature.

It is instructive to consider the observed increase of i with ageing under discharge and especially that due to pre-heating. Joshi has shown that the current in an ozoniser system is given by the following equation:—

$$i = \frac{V}{\frac{1}{JC_w \sum f} + \frac{1}{\frac{1}{R_g} + JC_g \sum f}} \quad \dots (1)$$

where C_w is the combined capacity due to inner and outer annular walls and C_g is the capacity of the gas in the annular space; $\sum f$ represents not only the frequency of A.C. supply and its harmonics, but also those produced under electric discharge due to V (*Curr. Sci.*, 1947, 16, 19). According to this equation, i should increase by an increase in any one or more of the quantities, $1/R_g$, C_g , C_w and $\sum f$. The ohmic current $1/R_g$ is a function of the number of ions per c.c. and their average velocity; these should not change sensibly with temperature *per se*. Since C_g is measured by the dielectric constant of the gas, which decreases with temperature, a change therein, due to heating cannot explain the observed rise of i by ageing. The dielectric constant of glass increases by 0.2% per degree rise in temperature and therefore on that account C_w might increase by about 11% over the operative temperature change adopted in this work. The corresponding rise in i , expected from equation (1), is, however, but a small part of the rise in i due to heating, viz., 100%

In conclusion, the author expresses his grateful thanks to Prof. S. S. Joshi for suggesting the problem and his kind interest during this investigation.

MAGNETO-CHEMICAL STUDIES IN VALENCY. PART IV. TETRAPOSITIVE NICKEL AS ALKALI NICKEL PERIODATES

BY PRIYADARANJAN RÂY AND BYOMKES SARMA

Preparation and properties of sodium and potassium nickel periodates, containing tetrapositive nickel, have been described. The compounds are represented by the formula, $\text{Na(K)NiO}_4 \cdot x\text{H}_2\text{O}$, apparently a mixed or double salt of ortho-periodic acid of which the hydrogen atoms are replaced by one alkali metal and one quadrivalent nickel atom. The determination of magnetic susceptibility, giving a very low moment value ($\mu_B = 1.1$), indicates, however, that the compounds belong to the class of penetration complexes having octahedral configuration of oxygen atoms around nickel with d^2sp^3 hybrid bonds. It is, therefore, assumed that $[\text{Ni}(\text{IO}_6)]$ is present as a univalent complex anion in their molecule. The diamagnetic character of alkali silver and alkali copper periodates containing tripositive silver and copper, as observed by Malatesta, has also been accounted for in a similar manner.

It has been reported by some previous workers that manganese, cobalt, copper and silver in their tervalent state can form double or complex periodates with periodates of alkali or other metals (cf. Berg, *Compt. rend.*, 1899, 128, 673; Price, *Amer. Chem. J.*, 1903, 30, 182; Urtis, *Rec. trav. chim.*, 1925, 44, 423; Malaprade, *Bull. soc. chim.*, 1935, v, 2, 359; 1936, v, 3, 361; 1936, 5, 582; *Compt. rend.*, 1937, 204, 979; Malatesta, *Gazzetta*, 1941, 71, 467, 580). Malatesta also measured the magnetic susceptibility of those periodates containing copper and silver in the tervalent state, and found them all to be diamagnetic. The manifestation of higher valencies by copper and silver in combination with periodates suggested that the element nickel might as well behave in a similar manner, particularly in view of the fact that this element was already known to exhibit a higher valency in the form of a black oxide and in the so-called niccolites. Furthermore, the preparation of a quadrivalent nickel molybdate in combination with alkali or alkaline earth molybdate by Hall (*J. Amer. Chem. Soc.*, 1907, 29, 692) supported this idea. These latter substances form fine purple-black crystalline compounds and, as has been shown in Part III of this series (Rây, Bhaduri and Sarma, this *Journal*, 1948, 25, 51) from a consideration of their magnetic properties, should be regarded as salts of complex heteropolymolybdic acid with tetrapositive nickel as the central atom. Guided by this analogy, we succeeded in preparing specimens of sodium and potassium nickel periodates with nickel atom in the tetrapositive state. The preparation and properties of these substances are described below.

It might, however, be mentioned here that Malaprade (*Compt. rend.*, 1937, 204, 979) also tried to prepare a nickel periodate with nickel in a higher valency state, but failed to obtain any positive result.

EXPERIMENTAL

Sodium Nickel Periodate.— $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (2 g.) dissolved in water was treated with a solution of sodium periodate, $\text{Na}_2\text{H}_2\text{IO}_6$ (5 g.). The mixture was heated nearly to

boiling and then oxidised by the addition of sodium persulphate (8 g.), added in small quantities at a time. The light green solution gradually turned darker in colour with separation of fine, dark purple, almost black crystals with shining metallic lustre. The crystals show a great tendency to adhere to the walls of the beaker in the form of a bright mirror, and are practically insoluble in cold water. They were washed first with dilute sodium persulphate solution and then with hot water. The crystals were dried in air. The substance emits an odour of ozonized oxygen in air and readily decomposes when heated. [Found : Ni, 18.20 ; Na, 6.99 ; I, 38.86, 40.20 ; O (total active), 24.35, O(Ni⁴⁺), 4.57, 4.78 ; H₂O (by difference), 5.5. NaNiO₆.H₂O requires Ni, 18.19 ; Na, 7.13 ; I 39.36, O (total active) 24.79 ; O(Ni⁴⁺), 4.96 ; H₂O, 5.6 per cent].

Nickel was estimated as nickel dimethylglyoxime after decomposition of the substance with SO₂ and HCl. Sodium was estimated as sodium sulphate in the filtrate from nickel. Iodine was estimated as silver iodide after decomposition and reduction of the substance with SO₂ and dilute sulphuric acid. The total active oxygen was determined from the amount of iodine liberated by the substance from an acid solution of potassium iodide. After making due allowance for the periodate radical, as determined from the amount of silver iodide, the valency of nickel was deduced from its oxygen equivalent.

Potassium nickel periodate was prepared like the corresponding sodium compound, using potassium periodate, KIO₄, and potassium persulphate in place of the sodium salts. It resembles its sodium analogue in properties. [Found : Ni, 17.78, 17.83 ; K, 12.16 ; I, 39.04, 38.63 ; O (total active), 23.77 ; O(Ni⁴⁺), 4.28 ; H₂O (by difference), 2.64. KNiO₆, 0.5H₂O requires Ni, 17.78 ; K, 11.84 ; I, 38.48 ; O (total active), 24.24 ; O(Ni⁴⁺), 4.85 ; H₂O, 2.73 per cent].

Malaprade (*loc. cit.*) oxidised nickel hydroxide, suspended in a mixture of potassium periodate and caustic potash solution, with potassium persulphate. A brown solution was obtained, from which, however, no compound could be isolated.

Measurements of Magnetic Susceptibility.—Measurements were made in a Gouy's balance with a field strength of 10.16×10^3 gauss.

Substance.	<i>t.</i>	$\chi_g \times 10^6$.	$\chi_M \times 10^6$.	$\chi_M^{corr} \times 10^6$.	μ_B .
NaNiO ₆ .H ₂ O	31°	1.284	415	510	1.11
KNiO ₆ .0.5H ₂ O	„	1.143	376	473.3	1.08

The diamagnetic correction for [IO₆]³⁻ was deduced from the measurement of susceptibility value of Na₃H₂IO₆ for which $\chi_g = -0.2933 \times 10^{-6}$ and $\chi_M = -86.22 \times 10^{-6}$. From this χ_M for [IO₆]³⁻ = -65.8×10^{-6} .

DISCUSSION

The magnetic moment values for the sodium and potassium periodates, described above, show that the tetrapositive nickel atom in these compounds cannot contain any unpaired electron. For, the observed moment value is less than even $1.73 \mu_B$, required for the presence of a single unbalanced electron on the basis of Bose-Stoner's formula. This

seems to suggest that the substances in the pure state would possibly be diamagnetic, the observed paramagnetic susceptibility of low moment value arising presumably from partial dissociation due to their temperature instability. The composition of these compounds, $\text{Na(K)Ni(IO)}_6 \cdot x\text{H}_2\text{O}$, corresponds apparently to a mixed salt of ortho-periodic acid, H_5IO_6 , the hydrogen atoms of which are replaced by one quadrivalent nickel and one alkali metal atom. But a quadrivalent nickel ion in the normal state should give a moment value of 4.9 Bohr due to four unpaired electrons, while the observed value indicates the absence of even a single unpaired electron. The diamagnetic character of alkali and alkaline-earth nickel molybdates with nickel in the quadrivalent state has been accounted for in part III (*loc. cit.*) as due to the formation by the nickel atom of a heteropoly-acid complex of the penetration type with d^2sp^3 hybrid octahedral bonds. In this it resembles the tripositive cobalt in all cobaltic complexes. The fact that the tetrapositive nickel and tripositive cobalt possess the same number of electrons justifies this assumption. In the present case of alkali nickel periodates, however, their very simple composition precludes any such attempt at representing them as heteropoly-acid complex of the above type. Nevertheless, their magnetic property demands that they should also be represented as a penetration complex with the tetrapositive nickel atom constituting the centre of a co-ordination octahedron with d^2sp^3 hybrid bonds. A quadrivalent nickel atom like those of its higher homologues, quadrivalent palladium and platinum, is likely to have a co-ordination number of six, resembling tervalent cobalt with which it is iso-electronic. This should make the complex diamagnetic. The very low moment value, as actually observed, is possibly due to a partial dissociation of these substances into Na(K)IO_4 and NiO_2 , as suggested above.

The possible structure of these alkali nickel periodates in the crystalline state may, therefore, be represented as follows. Each nickel, iodine or potassium atom is surrounded octahedrally by six oxygen atoms; and each oxygen is bound to one nickel, one iodine and one potassium atom, showing a co-ordination number of three. Every oxygen atom constitutes a common corner for all the three octahedra which possibly share edges with each other. The bonds between oxygen and nickel, as well as those between oxygen and iodine, are predominantly covalent, due to strong polarizing power of the highly positive nickel (quadrivalent) and iodine (heptavalent) atoms, while those between potassium and oxygen atoms are purely ionic. The compounds should, therefore, be represented by the formula, $\text{Na(K)[Ni}^{\text{IV}}(\text{IO}_6)]$.

A similar explanation can also be advanced in order to account for the diamagnetic character, as observed by Malatesta (*loc. cit.*), of the alkali-silver and alkali-copper periodates containing tripositive silver and copper atoms (*vide supra*). The composition of these compounds are represented by the formulae, $\text{M}_7\text{Cu}(\text{IO}_6)_2$ and $\text{M}_7\text{Ag}(\text{IO}_6)_2$, where M_7 may be Na_7 , K_7 , K_6H , Na_6H , or KHNa_5 . In these, the tervalent Ag or Cu atom is quadri-coordinated with oxygen in a planar square configuration forming dsp^2 hybrid bonds. For, a tervalent copper, being iso-electronic with bivalent nickel, is likely to show a co-ordination number of four. Similarly, a tripositive silver atom is already known to be quadri-coordinated like bivalent palladium with which it is iso-electronic (*cf.* Rây and Chakravarty, *J. Indian Chem. Soc.*, 1944, **21**, 47). Each iodine atom is

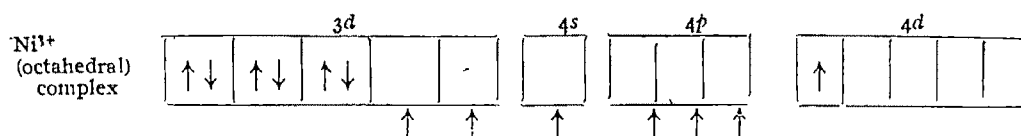
MAGNETO-CHEMICAL STUDIES IN VALENCY. PART V. VALENCY OF NICKEL, AND NATURE OF THE BOND IN ARSENICAL NICKEL ORES

BY PRIYADA RANJAN RÂY AND DWIJENDRA NATH SEN

Measurement of magnetic susceptibility of a specimen of arsenical nickel glance, NiAsS , and of a specimen of red nickel ore (kupfernickel), NiAs , gave moment values of $1.85\mu_B$ and $0.74\mu_B$ respectively. From this it has been concluded that in the former the nickel atom is in the tervalent state and it is covalently bound to arsenic atom in an octahedral configuration by means of d^2sp^3 hybrid bonds, while in the latter the bonds are metallic in character. The results are in good agreement with those deduced from a consideration of known interatomic distances and crystal structure determined by the X-ray method, as also with the general physical properties of the substances.

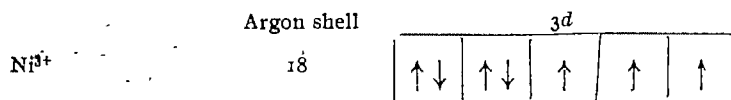
The valency state of the elements of the transitional series in their sulphide and arsenical ores, and the nature of linkage with which they bind the neighbouring sulphur and arsenic atoms, present a somewhat intriguing problem. Thus, for instance, iron pyrites, FeS_2 , which has been found by X-ray analysis to possess the characteristic pyrites structure with every iron atom bound octahedrally to six S-atoms (rather S_2) and each sulphur atom linked tetrahedrally to three iron atoms and one sulphur atom, is believed on the basis of their interatomic distances to consist essentially of covalent bonds with iron in the bivalent state. The fact that the substance is very feebly paramagnetic seems to support this idea, and Pauling ("The Nature of the Chemical Bond," 1940, p. 181) therefore assumes that the structure corresponds to the formation of $3d^24s4p^3$ bonds by Fe as in $[\text{Fe}(\text{CN})_6]^{4-}$. In hauerite, MnS_2 , which also crystallises in pyrites structure, it is argued from Mn—S interatomic distance, as determined by X-ray analysis, that the bonds are probably ionic, because the calculated octahedral covalent radius of bivalent manganese (1.26\AA approx.) is much lower than 1.55\AA deduced from the observed Mn—S distance of 2.59\AA . This is in good agreement with the result of magnetic measurement on the mineral, which gives a moment value of 6.1 Bohr for Mn (Elliot, *J. Amer. Chem. Soc.*, 1947, **59**, 1958). It differs widely from the value of $1.73\mu_B$ expected for d^2sp^3 hybrid covalent bonds as in manganocyanide, $[\text{Mn}(\text{CN})_6]^{4-}$. On the other hand, it agrees closely with the moment value of 5.92 Bohr of manganous ion.

In arsenical nickel glance, NiAsS , which also forms pyrites type of crystal, it is believed from the known values of interatomic distance that the bonds are of covalent d^2sp^3 type as in FeS_2 with the nickel atom in the tervalent state. On this basis it should give a moment value of one promoted electron as shown below :



In kupfernickel or red nickel ore, NiAs , which crystallises in the nickel arsenide type, each As-atom is bound to six Ni-atoms at the corners of a trigonal prism and each nickel atom is octahedrally surrounded by six As-atoms. Here too, the nickel atom is

believed to be tervalent from the measured Ni—As distance. If it also forms covalent bond of d^2sp^3 type, it should likewise give a moment value of one unpaired electron (1.73 Bohr) as shown above. On the other hand, if the bonds in these two minerals be essentially ionic in character, then a tervalent nickel ion should give a moment value corresponding to three unpaired electrons, i.e., 3.88 Bohr according to Bose-Stoner's formula, as is evident from the following representation :



With a view to determining the valency state of nickel atom and the nature of the bond in these two arsenical nickel ores, it was considered desirable to measure the magnetic susceptibility of the substances. A sample of nickel glance supplied by the Geological Survey of India and a very pure sample of kupfernickel, obtained several years ago from a German firm, were analysed and their susceptibilities measured. The results are recorded below.

Arsenical Nickel Glance.

TABLE I

Constituent.	Per cent.	Atom or mol. ratio.
Ni	22.69	0.3868
As	45.10	0.60
S	19.40	0.606
Fe	5.80	0.1038
Co	2.98	0.05
SiO ₂	3.59	0.06
Total	99.56	

It appears from the atomic ratio of the constituents that the ore is not a pure nickel glance of formula, NiAsS, or even Ni(Fe,Co)AsS with nickel partially substituted by iron and cobalt by isomorphous replacement. It seems that the ore is admixed with minerals of the type Ni(Fe,Co)As₂ or/and Ni(Fe,Co)S₂.

Magnetic Measurement (Gouy's balance).—The finely powdered ore (1.04977 g.) experienced a pull of 40.4 mg. at 31.5°, the length of the column being 9.3 cm. $H_{\max} = 10.16 \times 10^3$ gauss.

$$\chi_g = \frac{18.6 \times 40.4}{1.04977 \times 1.019 \times (10.16 \times 10^3)^2} = 7.1214 \times 10^{-6}$$

Diamagnetic corrections = $\chi_m \times 10^6$

As = -43, Ni = -12, Fe = -12, Co = -12, S = -15, SiO₂ = -22.

Diamagnetic correction for χ_g calculated from the above values and the analytical composition of the ore amounts to 0.428×10^{-6} .

Hence, χ_g (corrected) = $(7.1214 + 0.428) \times 10^{-6} = 7.549 \times 10^{-6}$.

χ_s = susceptibility of the substance containing Ni_{0.115} + Co_{0.002} + Fe_{0.102} = 1 g. atom

of the metals = $7.549 \times \frac{100}{0.5406} \times 10^{-6} = 1396 \times 10^{-6}$

(0.5406 represents the sum of the number of atoms of Ni, Co and Fe present in 100g. of the ore).

$$\mu \text{ (effective)} = 2.84 \sqrt{1396 \times 304.5 \times 10^{-6}} = 1.85 \text{ approx.}$$

Kupfernickel

(Found: Ni, 43.95. As 56.00: NiAs requires Ni, 43.80, As 56.20 per cent).

Magnetic Measurement.—The ore (1.54068g) gave a pull of 11.04 mg. at 31° , the length of the column being 9.1 cm.

$$\chi_g = \frac{18.20 \times 11.04}{1.54068 \times 1.019 \times (10.16 \times 10^3)^2} = 1.24 \times 10^{-6}.$$

$$\chi_m = 133.32 \times 1.24 \times 10^{-6} = 165.05 \times 10^{-6}.$$

$$\text{Diamagnetic corrections} = -55 \times 10^{-6}.$$

$$\chi \text{ (atom)} = (165.05 + 55) \times 10^{-6} = 220.05 \times 10^{-6}.$$

$$\mu \text{ (effective)} = 2.84 \sqrt{220 \times 304 \times 10^{-6}} = 0.74.$$

DISCUSSION

The nickel ore, kupfernickel, gives a very low moment value of 0.74 Bohr for nickel, which cannot be accounted for on the basis of ionic bond for the nickel atom either in the bi- ($\mu_B = 2.83$) or trivalent ($\mu_B = 3.88$) state. If the bonds be of the covalent d^2sp^3 type, the moment value for bivalent nickel would be 2.83 Bohr and for the trivalent complex it would be 1.73 Bohr. So the Ni—As bond in nickel arsenide or red nickel ore is neither ionic nor covalent, but presents a definite transition from the ionic type to the metallic character. This is further supported by the development of metallic or alloy-like properties in the compound, such as red metallic lustre, hardness or brittle character. Moreover, the fact that it can form solid solution with an excess of the transitional metals points in the same direction (Klemm and Shuth, *Z. anorg. allg. Chem.*, 1931, 203, 104). In consequence of the mutual interaction of the cation and the anion, the outermost electrons of the anion and cation lose their original hold on them and assume partially the character of metallic electrons. In fact, Goldschmidt (*Ber.*, 1927, 60, 1286) was the first to point out that due to such polarization phenomena metallic characters would be developed in substances of nickel arsenide structure, where a transitional metal of relatively small size was combined to a large readily polarizable element. The low co-ordination number of nickel in Ni—As, if we ignore the presence of two other nickel atoms as nearest neighbours, though reveals a departure from a purely metallic binding, nevertheless, that the structure is essentially metallic becomes evident from many of its properties, notably its magnetic moment. It may, therefore, be concluded that the Ni—As bond in kupfernickel is neither ionic nor covalent, but predominantly metallic representing a transition between the two, as a result of polarization. The question of valency of nickel atom does not, therefore, arise here.

The arsenical nickel glance, NiAsS, on the other hand, gives a fairly high magnetic moment value of 1.85 Bohr (approx.) showing that the bonds are not of the metallic type. The substance possesses a pyrites type of crystal structure, as stated before, and

it is known from the determination of interatomic distances by the X-ray method that the metal atom (Ni and therefore also Co and Fe which replace Ni isomorphously) occurs in the crystal in the tervalent state (cf. Pauling, "The Nature of the Chemical Bond", 1940, p. 183) and that as in pyrites each nickel atom is surrounded octahedrally by six AsS groups. If the bonds were ionic, the magnetic moment would have been much higher. For, tervalent nickel would give a moment value of 3.88 Bohr, corresponding to three unpaired electrons; tervalent cobalt would give a value of 4.90 Bohr, corresponding to four unpaired electrons; and tervalent iron would give a value of 5.92 Bohr, corresponding to five unpaired electrons on the basis of Bose-Stoner's formula. Hence, the moment value for the mineral under investigation would have been $0.715 \times 3.88 + 0.093 \times 4.90 + 0.192 \times 5.92 = 4.36$ Bohr approx. The determination of the radii of Ni atom in NiAsS by the X-ray method has shown that the metal is not only tervalent, but the structure of the crystal is essentially a homopolar one with some measure of metallic binding (cf. Pauling, *loc. cit.*). Hence, if the binding be covalent of the octahedral d^2sp^3 type, then the moment value for the substance under investigation should be 0.715×1.73 (corresponding to one unpaired electron in nickel) $+ 0.092 \times 0$ (diamagnetism for Co) $+ 0.192 \times 1.73$ (corresponding to one unpaired electron for Fe), *i.e.*, equal to 1.57 Bohr approx. Tervalent nickel, cobalt and iron in octahedral complexes with d^2sp^3 bonds are known to show the moment values of 1.73, 0, and 1.73 respectively. Thus the calculated value of 1.57 Bohr for the mineral approaches the observed value of 1.85. The latter is, however, somewhat higher. This is presumably due to the presence of impurities like $Ni^{II}S_2$ and $Fe^{IV}As_2$, as already discussed in connection with the analytical results. The valences of the metal atoms in these substances, as indicated in their symbols, are those deduced from their interatomic distances by X-ray measurement (cf. Pauling, *loc. cit.*). The moment value of each of these substances is given by 2.83 Bohr, corresponding to the presence of two unpaired electrons, as the metal atoms in them are known to form octahedral complexes with d^2sp^3 bonds. Besides, it may also be pointed out here that CoS_2 , which might as well be present as an impurity in the nickel glance under examination, has been found to be ferromagnetic below 130° (Haraldson and Klemm, *Z. anorg. allg. Chem.*, 1935, 223, 409). The presence of a slight trace of CoS_2 as an impurity will, therefore, considerably enhance the moment value of the arsenical nickel glance.

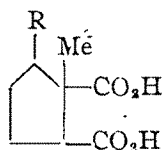
It can thus be established from the magnetic measurement that in arsenical nickel glance, the metal-metalloid binding is essentially covalent of the octahedral d^2sp^3 type and the nickel atom is in the tervalent state as already suggested from a consideration of their interatomic distances by Pauling (*loc. cit.*).

STUDIES IN THE CYCLOPENTANE SERIES. PART III.* EXPERIMENTS TOWARDS THE SYNTHESIS OF WIELAND'S C₁₃-ACID IN PROPER STEREOCHEMICAL FORMS

BY RANAJIT SEN-GUPTA AND PHANINDRA CHANDRA DUTTA

A method for the synthesis of 4-(1:5-dimethylhexyl)-5-methyl- Δ^1 -cyclopenten-1:5-dicarboxylic acid is described, which on reduction and the oxidation of the isopropyl group is expected to lead to the desired C₁₃ acid.

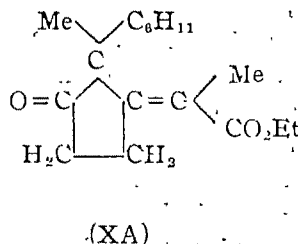
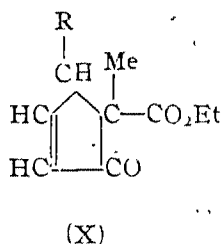
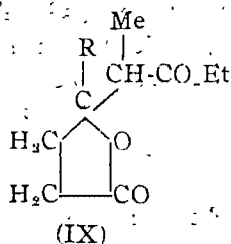
In Part I of this series (Dutta, *J. Indian Chem. Soc.*, 1940, 17, 611), two different routes have been developed for the synthesis of 1-methylcyclopentane-1:2-dicarboxylic acid in different stereoisomeric forms. The one, which appeared to be the most promising at that time, started from $\alpha\delta$ -dibromo- α -methylvaleric acid. Being encouraged by the preliminary success in the case of simple cyclopentane derivative, attention was first directed to apply this method to the synthesis of the following acid.



Unfortunately the attempts in this direction could not be pushed to a successful issue. The results of these investigations have been embodied in Part II (Dutta, *J. Indian Chem. Soc.*, 1942, 19, 79).

In the second method, ethyl 2-methylcyclopentanone-2-carboxylate has been utilised to synthesise the corresponding cyclopentane dicarboxylic acids. For the present purpose, the corresponding compound should be ethyl 2-methylcyclopentan-3-(1:5-dimethylhexyl)-1-one-2-carboxylate, for which, however, no feasible method of synthesis could then be devised. We are encouraged to reopen this subject after a pretty long time in view of the publication of an interesting paper (*J. Amer. Chem. Soc.*, 1944, 66, 4) on the synthesis of dihydrojasmonone. It utilises the property of the ready formation of cyclopentenones from γ -lactones on treatment with phosphorus pentoxide.

An analysis of this method leads to the following considerations. If the lactone of the following structure be subjected to this process of ring-closure, two compounds (X, XA) are theoretically possible.

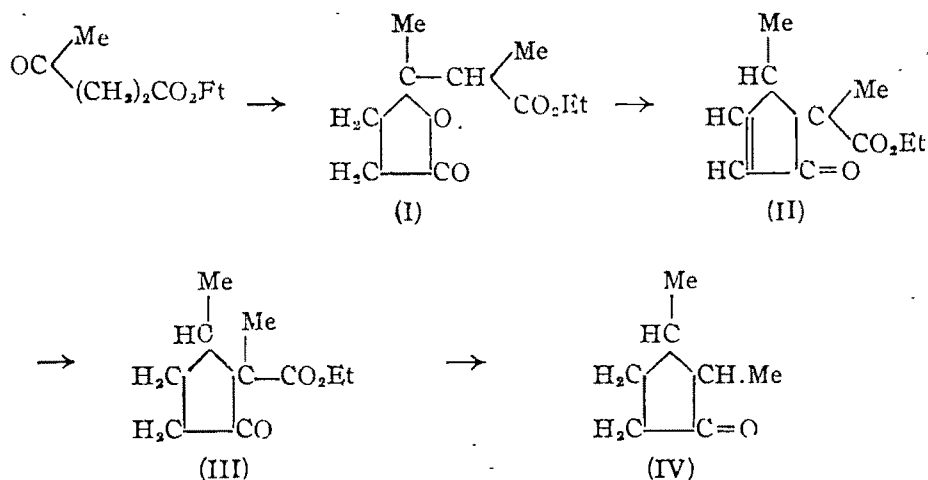


The theoretical considerations strongly favour the formation of (X), for the α -hydrogen atom, rendered active by the carbethoxyl group, will play its usual part in the formation.

* A preliminary note appeared in *Science & Culture*, 1944, 10, 355

tion of the carboxylic ring. This contention has been fully substantiated as subsequent investigations will show.

Before proceeding with the main scheme of work, it has been thought desirable to make pilot experiments with more easily available materials. The scheme followed in this case is outlined below

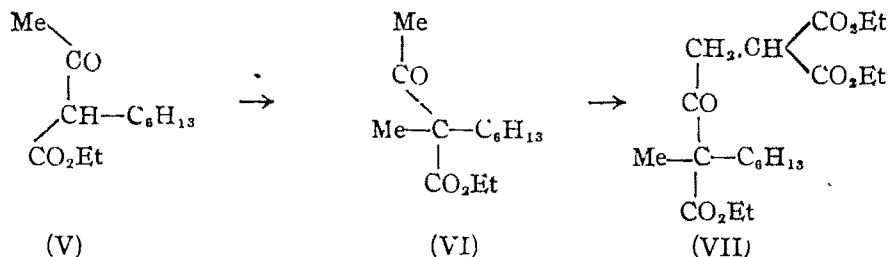


Ethyl levulinate condenses smoothly with ethyl α -bromopropionate in presence of zinc to give the lactone (I). This on distillation in high vacuum over P_2O_5 leads to the formation of the keto-ester (II) in poor yield (5%), though a considerable portion of the lactone is recovered unchanged. From the nature of the reaction it appears that the formation of the ketone is appreciable in the beginning, but the secondary reactions intervene with considerable tarrification. The unsaturated keto-ester assumes a light green tinge on standing overnight. It absorbs hydrogen catalytically quite readily and the reduced product (III) on hydrolysis gives dimethylcyclopentanone (IV) which is characterised by its boiling point, odour and a well-defined semicarbazone. The formation of (IV) completely rules out the formation of the other theoretical possibility, which would produce under identical conditions an acidic product.

Returning to the main scheme of work, we have synthesised the lactone (IX) by the action of ethyl α -bromopropionate on ethyl ester (VIII) of the long-chain keto-acid (Mukherjee, *J. Indian Chem. Soc.*, 1947, **24**, 425; *Science & Culture*, 1941-42, **7**, 58). The keto-ester (VIII) has been prepared according to Mukherjee with considerable modifications in the various steps of the process. We record briefly the methods of preparation of a few compounds first prepared by him, as some of the physical data are quite at variance with those obtained in the short note published by Mukherjee in the *Science & Culture*. We have also isolated the keto-acid in a solid form melting at $47-48^\circ$.

The *nor*-dihydrocitronellic acid (VIIA) required in this scheme has been prepared by the condensation of isohexyl iodide with ethyl methylmalonate and subsequent hydrolysis. The acid chloride of the above reacts with diazomethane in ethereal solution to give the bromomethyl-ketone (VIIB) (Dutta and Mitter, *Science & Culture*, 1943-44, **9**, 505). This condenses with malonic ester and the condensation product (VIIC) on

alkaline hydrolysis and decarboxylation gives the keto-acid (VIII) in a very good yield. Because of the lengthy steps in the synthesis of this acid, we have tried the following scheme.

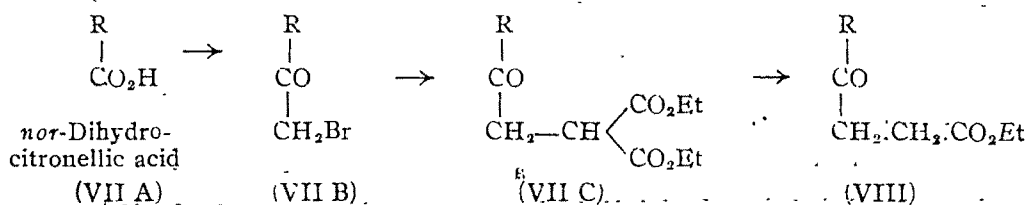


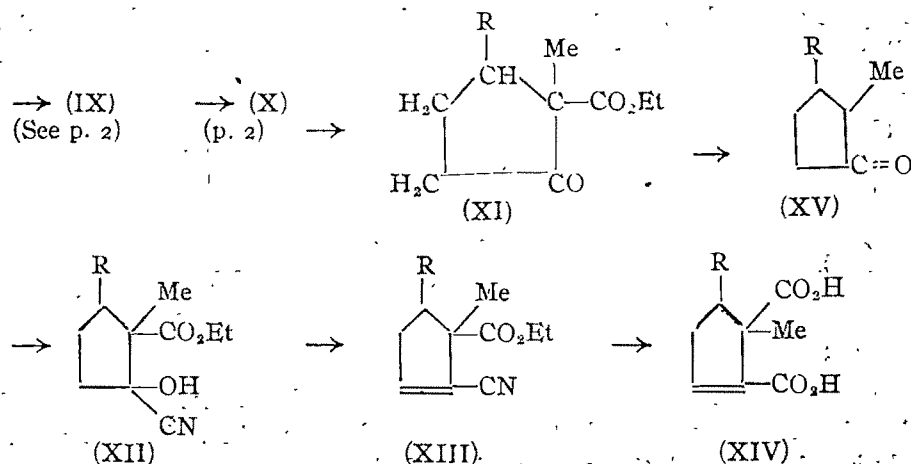
The two hydrogen atoms in acetoacetic ester can be replaced quite smoothly by isohexyl and methyl groups with the formation of (V) and (VI). The bromination of the disubstituted ester and the condensation of the bromo-ester with ethyl malonate proceeds quite readily. The hydrolysis of the condensation product proved an insurmountable difficulty. Recently an excellent method has been developed by P. C. Mukherjee in our laboratory (private communication) for this purpose.

Another method devised after Cason (*J. Amer. Chem. Soc.*, 1944, **62**, 46) consists of the condensation of the half-ester chloride of succinic acid with methylheptyl magnesium chloride (Robinson, *J. Chem. Soc.*, 1937, 1581) in presence of fused cadmium chloride. No keto-ester could be isolated in this case.

The ethyl ester (VII) of the keto-acid reacts smoothly with ethyl α -bromopropionate in presence of zinc to give the desired lactone (IX) together with a considerable amount of the high boiling residue. This on heating with P_2O_5 in vacuum gives the unsaturated keto-ester (X) in a very poor yield. It readily takes up hydrogen catalytically to give (XI). On hydrolysis with concentrated hydrochloric acid in a sealed tube this gives methylisooctylcyclopentanone (XV), the identity of which has been established with that synthesised by Mukherjee (*loc. cit.*) through its semicarbazone. The saturated keto-ester (XI) adds up one molecule of hydrocyanic acid and the cyanohydrin (XII) is then dehydrated with an excess of thionyl chloride and pyridine to lead to (XIII) mixed with sulphur compounds, the latter being removed by refluxing with precipitated copper in benzene solution. The unsaturated cyano-ester (XIII) is then hydrolysed by prolonged heating with hydrochloric acid in a sealed tube. The acidic component (XIV) from the product of hydrolysis is isolated in a very poor yield as a thick oil, which does not solidify even on long standing. Unfortunately no suitable solvent could be found to induce its crystallisation. This on reduction of the double bond and oxidation of the isopropyl group is expected to lead to Wieland's C_{15} -acid.

The main scheme of work is graphically represented below :





(In all the formulae $\text{R} = -\text{CH}(\text{Me})-(\text{CH}_2)_3-\text{CH}(\text{Me})_2$.

(*iso*-octyl)

Because of the disturbing effect of the *iso*-octyl group in the normal course of reactions, we have developed a new method to introduce the levulinic acid side-chain through a different route and this will form the subject matter of the next communication.

EXPERIMENTAL

Lactonic Ester of Ethyl α -Methyl- β -hydroxy- β -methyladipate (I).—Ethyl levulinate (15 g.) was dissolved in benzene (35 c.c.) to which zinc wool (20 g.) and ethyl bromopropionate (18 c.c.) and a crystal of iodine were added. On warming the reaction started and when the vigour of the reaction had subsided (10 minutes) it was heated on the water-bath for 2 hours. On cooling, it was decomposed with ice and acid. The benzene layer was washed with dilute ammonia solution and water. On distillation the lactone passed over at 136°/6 mm., yield 14 g. (Found : C, 60.0; H, 7.6. $\text{C}_{10}\text{H}_{16}\text{O}_4$ requires C, 60.0; H, 8.0 per cent).

Ethyl 2:3-Dimethyl- Δ^4 -cyclopentenone-2-carboxylate (II).—The above lactonic ester (15 g.) was added to phosphorus pentoxide (8 g.) when the mixture became very hot. Next it was heated in an oil-bath in high vacuum. The product gradually distilled and the distillate was collected (8 g.). It was again distilled and a small fraction (0.5 g.) was collected, which passed over at 90°-95°/6 mm. as a light, clear oil having a characteristic smell and assuming a green colour on standing. The major portion (6 g.) consisted of the unchanged lactone. (Found : C, 65.4; H, 7.3 $\text{C}_{10}\text{H}_{14}\text{O}_3$ requires C, 65.9; H, 7.7 per cent).

A portion of the oil was treated with semicarbazide hydrochloride in presence of sodium acetate and the semicarbazone separated after a week in the form of sandy crys-

tals. It crystallised from dilute alcohol as shining crystals with a yellowish tinge. It decomposed at $212-15^{\circ}$.

2:3-Dimethylcyclopentanone (IV).—The above unsaturated ester (0.7 g.) which was freshly distilled, was shaken with hydrogen in presence of platinum catalyst (0.1 g.). Absorption of hydrogen was complete in an hour and the catalyst settled down. It was filtered off and the saturated ester was obtained boiling at $90-92^{\circ}/6$ mm. as a clear, mobile oil having a camphoraceous odour. This ester (0.6 g.) was hydrolysed with hydrochloric acid (conc., 5 c.c.) for 8 hours. On cooling, the solution was extracted with ether thoroughly and on removal of the ether, a small quantity of an oil remained which on distillation gave a fraction (0.2 g.) at $140^{\circ}-150^{\circ}$ and this immediately gave the semicarbazone as shining sandy crystals, m. p. $179-80^{\circ}$ after recrystallisation from spirit. (Found: N, 25.4. $C_8H_{12}ON_3$ requires N, 24.8 per cent).

Ethyl isoHexylacetoacetate (V).—Sodium (5.5 g.), dissolved in alcohol (70 c.c.), was treated with acetoacetic ester (32 g.). Next *isohexyl iodide* (50 g.) was added and the solution refluxed for 8 hours. On working up the reaction mixture, the required ester passed over at $120^{\circ}/9$ mm, yield 46 g. (Found: C, 76.5; H, 10.4. $C_{12}H_{22}O_3$ requires C, 67.3; H, 10.3 per cent).

Ethyl Methylisohexylacetoacetate (VI).—Sodium salt of the above ester was prepared from sodium (5.6 g.), the ester (45 g.) in benzene (150 c.c.). On treatment with methyl iodide in large excess, a clear mobile liquid boiling at $118^{\circ}/7$ mm. was obtained, yield 31 g. (Found: C, 68.5; H, 10.5. $C_{13}H_{24}O_3$ requires C, 68.4; H, 10.4 per cent).

Ethyl δ -isoHexyl- γ -keto-hexoate (VIII).—*nor*-Dihydrocitronellic acid was prepared in quantity through the condensation of *isohexyl iodide* with ethyl methylmalonate and subsequent hydrolysis of the same. The acid chloride, prepared through the action of PCl_3 , was allowed to react with excess of diazomethane in ethereal solution. To the diazo-ketone was added hydrobromic acid and the bromoketone, thus obtained, condensed smoothly with malonic ester to give (VII). This ester (22 g.) was dissolved in spirit (80 c.c.) to which was added caustic potash (12 g.) in water (20 c.c.) and the whole was refluxed for 6 hours, when a clear solution was obtained. Next, alcohol was removed on the water-bath and from the alkaline solution, the dibasic acid was regenerated on acidification and extraction with ether. This on decarboxylation at 190° for about 15 minutes gave the monocarboxylic acid, passing over at $160^{\circ}-165^{\circ}/5$ mm., yield 14 g. (Mukherjee, *loc. cit.*, b. p. $150^{\circ}/5$ mm.). It solidified to long needles, m. p. $47-48^{\circ}$. The ethyl ester was prepared by refluxing the acid (12 g.) with a mixture of alcohol (30 c.c.) and sulphuric acid (1.5 c.c.) for 12 hours on a boiling water-bath. On working up in the usual way, the ethyl ester passed over at $130-32^{\circ}/5$ mm. (Mukherjee, *loc. cit.*, b. p. $122^{\circ}/6$ mm.), yield 12 g. (Found: C, 69.7; H, 11.1. $C_{14}H_{26}O_3$ requires C, 69.4; H, 10.7 per cent).

Reformatsky's Reaction with the Ester (VIII) and *Ethyl α -Bromopropionate* leading to the Lactone (IX).—This was prepared by heating on the water-bath a mixture of zinc wool (20 g.), the keto-ester (24 g.) and ethyl α -bromopropionate (15 c.c.) and benzene (60 c.c.) in presence of a crystal of iodine. Reaction started after sometime and when the vigour of the initial reaction was over, it was further heated for an hour. On cooling, a further

lot of zinc wool (10 g.) and bromo-ester (10 c.c.) were added and the mixture was refluxed for another hour. The solution became very thick and assumed a light green colour. On working up the mixture, the lactone was obtained boiling at $174^{\circ}/4$ mm. (Mukherjee, b. p. $170^{\circ}/4$ mm.), yield 14 g.

Ethyl 2-Methyl-3-isooctyl- Δ^4 -cyclopentenone-2-carboxylate (X).—The above lactone (IX, 10 g.) was heated in vacuum at 130° - 140° for 10 minutes with phosphorus pentoxide (5 g.). The reaction mixture turned brown. Next it was cooled and decomposed with ice. It was extracted with ether and the ethereal solution was washed with sodium carbonate solution. On working up, a fraction (1.6 g.) was collected at 140° - $155^{\circ}/4$ mm. and the unchanged lactone was recovered at 160° - $170^{\circ}/4$ mm. (5 g.). This was again treated with P_2O_5 (2.5 g.) and worked in the identical way. The combined lower boiling portions (2.5 g.) were redistilled when the keto-ester came over at $145^{\circ}/4$ mm., yield 1.5 g. (Found: C, 72.4; H, 10.1. $C_{17}H_{28}O_3$ requires C, 72.8; H, 10.1 per cent).

No semicarbazone could be prepared from this keto-ester.

Ethyl 2-Methyl-3-isooctylcyclopentanone-2-carboxylate (XI).—The above unsaturated ester (X, 2.9 g.) was dissolved in glacial acetic acid (10 c.c.) and the solution was shaken in an atmosphere of hydrogen with platinum oxide (0.2 g.). Absorption of hydrogen was complete in 2 hours (ca. 265 c.c.). It was worked up in the usual way and on distillation it passed over at 150° - $155^{\circ}/8$ mm., yield quantitative. (Found: C, 71.9; H, 10.3. $C_{17}H_{30}O_3$ requires C, 72.3; H, 10.6 per cent).

2-Methyl-3-isooctylcyclopentanone (XV).—The ester (XI, 1.5 g.) was hydrolysed with hydrochloric acid (conc., 10 c.c.) for 36 hours in a sealed tube at 130° - 140° . On working up, a small fraction (0.2 g.) was isolated boiling at 115° - $125^{\circ}/6$ mm. and another fraction came over at higher temperature leaving a considerable quantity of tarry residue in the flask. It was directly converted into semicarbazone which separated slowly as sandy crystals along with an oily matter. On removal of the oily matter on a porous plate, the residue was crystallised from dilute alcohol, m. p. 178 - 79° (Mukherjee, b. p. 180 - 81°). (Found: N, 15.0. $C_{15}H_{26}ON_3$ requires N, 15.7 per cent).

5-Methyl-5-carbethoxy-4-isooctyl- Δ^1 -cyclopentenyl Cyanide (XIII).—The above keto-ester (XI, 2.5 g.) was treated at -10° with liquid hydrocyanic acid, generated from potassium cyanide (7 g.) and sulphuric acid (H_2SO_4 , 7 c.c., H_2O , 10 c.c.) in presence of a drop of potassium cyanide solution. The mixture was allowed to stand in an ice-chest overnight. It was then acidified and the excess of hydrocyanic acid was removed in suction. It was extracted with ether and dried thoroughly in vacuum after removal of the solvent. The residue (2.5 g.) was dissolved in pyridine (5 c.c.) and cooled in a freezing mixture. To this was added thionyl chloride (3 c.c.) and the mixture was allowed to stand in ice for an hour. Next, it was heated on the water-bath for 2 hours. The mixture was decomposed with ice and extracted with ether. The ethereal extract was washed with acid and alkali and the residue left on evaporation of the solvent was again treated with precipitated copper in benzene solution. On working up in the usual way, the unsaturated cyano-ester was obtained boiling at 145° - $150^{\circ}/2$ mm., yield 1.3 g. The product was slightly yellowish and a few drops of unchanged keto-ester were collected as a forerun. (Found: N, 4.4. $C_{18}H_{26}O_2N$ requires N, 4.8 per cent).

4-isoOctyl-5-methyl- Δ^1 -cyclopenten-1:5-dicarboxylic Acid (XIV).— The above unsaturated cyano-ester (XIII, 1.2 g.) was heated with hydrochloric acid (conc., 10 c.c.) in a sealed tube for 12 hours at 130°-140° and for another 12 hours at 150°. There was an appreciable tarrification, and the residue was taken up in ether. The acidic products were washed with sodium bicarbonate solution. On acidification of the alkaline solution, a thick liquid separated out. This was extracted with ether. On removal of the solvent, it was decolorised with animal charcoal in dilute alcoholic solution. On working up, a pale yellow, viscous liquid remained in the flask which could not be converted into solid by keeping in contact with different solvents. The product was, however, free from nitrogen.

Our best thanks are due to Dr. P. C. Mitter, Palit Professor of chemistry (retired) for his kind interest in this piece of investigation. We also take this opportunity of thanking Mr. N. N. Ghosh and Mr. C. N. Bhar for micro-analysis of some the compounds.

SIR P. C. RAY FELLOW'S LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY,
CALCUTTA.

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PHYSICO-CHEMICAL STUDIES ON THE COMPOSITION OF COMPLEX METALLIC FERRO AND FERRICYANIDES. PART VI. CONDUCTOMETRIC STUDIES ON THE COMPOSITION OF CADMIUM FERROCYANIDE

BY ABANI K. BHATTACHARYA AND HARISH C. GAUR

Studies on the composition of cadmium ferrocyanide have been further extended. Conductometric studies support the results of the thermometric and potentiometric studies. The compound $K_2CdFeCy_6$ is formed, but the composition is also influenced by hydrolysis and adsorption.

'Analar' (B. D. H.) reagents were used. Preparation of standard solutions (Part IV, this journal, 1948, 26, 185) and all further dilutions were made with conductivity water. The arrangement was similar to the one used previously (Part III, this journal, 1948, 26, 27) except that the induction coil was replaced by a low frequency oscillator ($\nu = 1240$). The titrations were similarly carried out in the aqueous and aqueous-alcoholic media. The conductance after each addition was also corrected (*loc. cit.*). With different concentrations of the two salt solutions, the titrations were carried by the direct and the reverse methods, i.e., when cadmium sulphate from the burette was added to potassium ferrocyanide taken in the cell, and *vice versa*.

$M/5.40$ -cadmium sulphate would be referred as A/1-cadmium sulphate solution, and $M/5.10$ solution of potassium ferrocyanide, as A/1-potassium ferrocyanide solution.

Direct Conductometric Titrations

TABLE I

A/10- K_4FeCy_6 soln. = 10 c.c. Alcohol = nil. (Fig. 1, curve 1).

A/1- $CdSO_4$ added.	Total vol	Corr conduc. $\times 10^3$.	A/1- $CdSO_4$ added	Total vol.	Corr conduc $\times 10^3$
0.0 c.c.	10.0 c.c.	29.24 mhos	1.3 c.c.	11.3 c.c.	26.34 mhos
0.2	10.2	27.20	1.4	11.4	20.73
0.4	10.4	26.00	1.5	11.5	21.28
0.6	10.6	24.38	1.6	11.6	21.81
0.8	10.8	22.68	1.7	11.7	22.23
0.9	10.9	21.80	1.8	11.8	22.90
1.0	11.0	21.08	1.9	11.9	23.56
1.1	11.1	20.00	2.0	12.0	24.14
1.2	11.2	19.82			

TABLE II

A/10-K₄FeCy₆ soln.=9 c.c. Alcohol=1 c.c. (Fig. 1, curve 2).

A/1-CdSO ₄ added.	Total vol.	Corr. conduc. × 10 ³ .	A/1-CdSO ₄ added.	Total vol.	Corr. conduc. × 10 ³ .
0.0 c.c.	10.0 c.c.	18.18 mhos	1.0 c.c.	11.0 c.c.	13.25 mhos
0.2	10.2	17.39	1.1	11.1	13.46
0.4	10.4	16.38	1.2	11.2	13.91
0.6	10.6	15.43	1.3	11.3	14.40
0.7	10.7	14.87	1.4	11.4	14.59
0.8	10.8	14.31	1.5	11.5	15.13
0.9	10.9	13.80	1.6	11.6	15.54

TABLE III

A/10-K₄FeCy₆=8 c.c. Alcohol=2 c.c. (Fig. 1, curve 3).

A/1-CdSO ₄ added.	Total vol.	Corr. conduc. × 10 ³ .	A/1-CdSO ₄ added.	Total vol.	Corr. conduc. × 10 ³ .
0.0 c.c.	10.0 c.c.	12.66 mhos	0.9 c.c.	10.9 c.c.	9.69 mhos
0.2	10.2	12.14	1.0	11.0	10.09
0.3	10.3	11.77	1.1	11.1	10.32
0.4	10.4	11.49	1.2	11.2	10.63
0.5	10.5	11.24	1.3	11.3	10.92
0.6	10.6	10.76	1.4	11.4	11.24
0.7	10.7	10.39	1.5	11.5	11.56
0.8	10.8	10.09			

TABLE IV

A/10-K₄FeCy₆ soln.=10 c.c. Alcohol=nil. (Fig. 2, curve 4).

A/2-CdSO ₄ added.	Total vol.	Corr. conduc. × 10 ³ .	A/2 CdSO ₄ added.	Total vol.	Corr. conduc. × 10 ³ .
0.0 c.c.	10.0 c.c.	28.17 mhos	2.2 c.c.	12.2 c.c.	19.52 mhos
0.4	10.4	26.87	2.3	12.3	19.37
0.8	10.8	25.44	2.4	12.4	19.68
1.2	11.2	23.83	2.5	12.5	20.00
1.6	11.6	22.31	2.6	12.6	20.32
1.8	11.8	21.45	2.8	12.8	20.92
2.0	12.0	20.51	3.0	13.0	21.67
2.1	12.1	20.00			

TABLE V

A/10-K₄FeCy₆=9 c.c. Alcohol=1 c.c. (Fig. 2, curve 5).

A/2-CdSO ₄ added.	Total vol.	Corr. conduc. $\times 10^3$	A/2-CdSO ₄ added.	Total vol.	Corr. conduc. $\times 10^3$
0.0 c.c.	10.0 c.c.	18.87 mhos.	1.9 c.c.	11.9 c.c.	14.42 mhos.
0.4	10.4	18.24	2.0	12.0	14.20
0.8	10.8	17.42	2.1	12.1	14.40
1.0	11.0	16.92	2.2	12.2	14.70
1.2	11.2	16.58	2.4	12.4	15.22
1.4	11.4	15.84	2.6	12.6	15.65
1.6	11.6	15.37	2.8	12.8	16.10
1.8	11.8	14.84	3.0	13.0	16.67

TABLE VI

A/10-K₄FeCy₆=8 c.c. Alcohol=2 c.c. (Fig. 2, curve 6).

A/2-CdSO ₄ added.	Total vol.	Corr. conduc. $\times 10^3$	A/2-CdSO ₄ added.	Total vol.	Corr. conduc. $\times 10^3$
0.0 c.c.	10.0 c.c.	13.42 mhos.	1.8 c.c.	11.8 c.c.	10.93 mhos
0.4	10.4	13.00	1.9	11.9	11.12
0.8	10.8	12.48	2.0	12.0	11.27
1.0	11.0	12.16	2.2	12.2	11.68
1.2	11.2	11.79	2.4	12.4	12.16
1.4	11.4	11.40	2.6	12.6	12.53
1.6	11.6	10.94	2.8	12.8	12.99
1.7	11.7	10.78			

Reverse Titrations

TABLE VII

A/10-CdSO₄ soln.=10 c.c. Alcohol=nil. (Fig. 3, curve 7).

A/2-K ₄ FeCy ₆ added.	Total vol.	Corr. conduc. $\times 10^4$	A/2-K ₄ FeCy ₆ added	Total vol.	Corr. conduc. $\times 10^4$
0.0 c.c.	10.0 c.c.	90.12 mhos	1.7 c.c.	11.7 c.c.	173.2 mhos
0.2	10.2	104.0	1.8	11.8	177.4
0.4	10.4	115.5	1.9	11.9	190.4
0.6	10.6	124.0	2.0	12.0	205.1
0.8	10.8	129.4	2.2	12.2	233.0
1.0	11.0	139.3	2.3	12.3	246.0
1.2	11.2	149.3	2.4	12.4	258.0
1.4	11.4	159.6	2.5	12.5	272.8
1.6	11.6	169.4			

TABLE VIII

A/10-CdSO₄=9 c.c. Alcohol=1 c.c. (Fig. 3, curve 8).

A/2-K ₄ FeCy ₆ added.	Total vol.	Corr. conduc. × 10 ⁴	A/2-K ₄ FeCy ₆ added.	Total vol.	Corr. conduc. × 10 ⁴
0.0 c.c.	10.0 c.c.	57.14 mhos	1.4 c.c.	11.4 c.c.	120.0 mhos
0.2	10.2	67.55	1.5	11.5	124.2
0.4	10.4	76.47	1.6	11.6	127.6
0.6	10.6	82.79	1.7	11.7	136.1
0.8	10.8	91.15	1.8	11.8	146.6
1.0	11.0	100.9	1.9	11.9	157.7
1.2	11.2	110.4	2.0	12.0	168.5

TABLE IX

A/10-CdSO₄=8 c.c. Alcohol=2 c.c. (Fig. 3, curve 9).

A/2-K ₄ FeCy ₆ added.	Total vol.	Corr. conduc. × 10 ⁴	A/2-K ₄ FeCy ₆ added.	Total vol.	Corr. conduc. × 10 ⁴
0.0 c.c.	10.0 c.c.	34.48 mhos.	1.4 c.c.	11.4 c.c.	90.48 mhos
0.2	10.2	42.50	1.5	11.5	96.63
0.4	10.4	49.52	1.6	11.6	106.4
0.6	10.6	57.29	1.7	11.7	115.3
0.8	10.8	65.45	1.8	11.8	122.2
1.0	11.0	73.82	1.9	11.9	131.0
1.2	11.2	82.96	2.0	12.0	139.6
1.3	11.3	87.60			

TABLE X

A/10-CdSO₄=10 c.c. Alcohol=0 nil. (Fig. 4, curve 10).

A/4-K ₄ FeCy ₆ added.	Total vol.	Corr. conduc. × 10 ⁴	A/4-K ₄ FeCy ₆ added.	Total vol.	Corr. conduc. × 10 ⁴
0.0 c.c.	10.0 c.c.	84.82 mhos	3.4 c.c.	13.4 c.c.	164.4 mhos.
0.4	10.4	97.21	3.6	13.6	168.9
0.8	10.8	108.5	3.7	13.7	174.5
1.2	11.2	117.9	3.8	13.8	179.4
1.6	11.6	123.4	3.9	13.9	186.5
2.0	12.0	132.4	4.0	14.0	193.2
2.4	12.4	141.4	4.2	14.2	205.9
2.8	12.8	150.5	4.4	14.4	218.2
3.2	13.2	159.7			

TABLE XI

A/10-CdSO₄=9 c.c. Alcohol=1 c.c. (Fig. 4, curve 11).

A/4-K ₄ FeCy ₆ added.	Total vol.	Corr. conduc. × 10 ⁴ .	A/4-K ₄ FeCy ₆ added.	Total vol.	Corr. conduc. × 10 ⁴ .
0.0 c.c.	10.0 c.c.	54.35 mhos.	3.2 c.c.	13.2 c.c.	126.3 mhos
0.4	10.4	65.00	3.3	13.3	131.1
0.8	10.8	73.98	3.4	13.4	136.0
1.2	11.2	81.76	3.5	13.5	141.8
1.6	11.6	89.92	3.6	13.6	145.5
2.0	12.0	98.36	3.8	13.8	156.8
2.4	12.4	108.8	4.0	14.0	168.0
2.8	12.8	118.5			

TABLE XII

A/10-CdSO₄=8 c.c. Alcohol=2 c.c. (Fig. 4, curve 12).

A/4-K ₄ FeCy ₆ added.	Total vol.	Corr. conduc. × 10 ⁴ .	A/4-K ₄ FeCy ₆ added.	Total vol.	Corr. conduc. × 10 ⁴ .
0.0 c.c.	10.0 c.c.	32.05 mhos.	2.8 c.c.	12.8 c.c.	90.14 mhos
0.4	10.4	40.79	3.0	13.0	96.29
0.8	10.8	48.00	3.2	13.2	105.6
1.2	11.2	55.44	3.4	13.4	114.5
1.6	11.6	64.45	3.6	13.6	122.5
2.0	12.0	72.73	3.8	13.8	132.1
2.4	12.4	81.59	4.0	14.0	141.4
2.6	12.6	86.31			

DISCUSSION

Considering the strength of the solutions of cadmium sulphate ($M/5.40$) and potassium ferrocyanide ($M/5.10$), theoretical titre values for 10 c.c. of potassium ferrocyanide solution, for the formation of the compounds $K_2CdFeCy_6$, Cd_2FeCy_6 and $K_2Cd_3(FeCy_6)_2$ in direct titrations are respectively 10.58, 21.16, and 15.87 c.c. of cadmium sulphate solution. The theoretical titre values for 10 c.c. of cadmium sulphate solution for the formation of the above compounds in the reverse titrations would be 9.45, 4.72 and 6.3 c.c. of potassium ferrocyanide solution.

The observed titre values in aqueous medium in direct titrations are slightly higher than the theoretical titre values required for the formation of the compound $K_2CdFeCy_6$. In the reverse titrations the observed value in aqueous medium is lower than the theo-

FIG. 1.

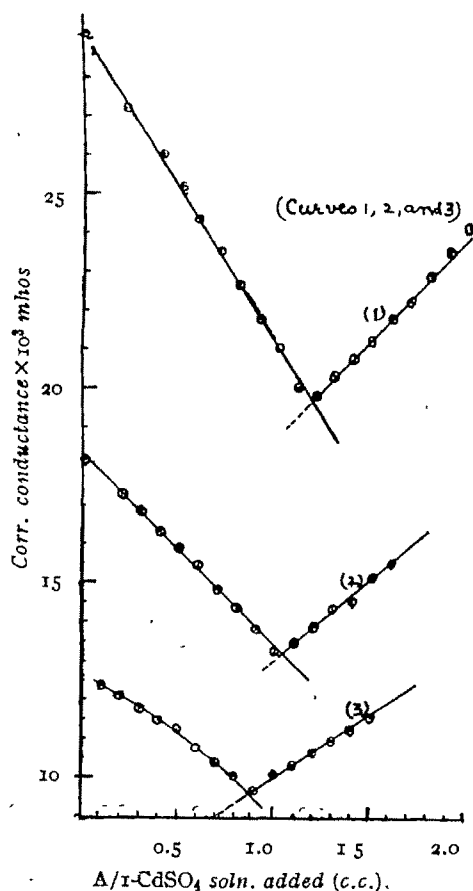
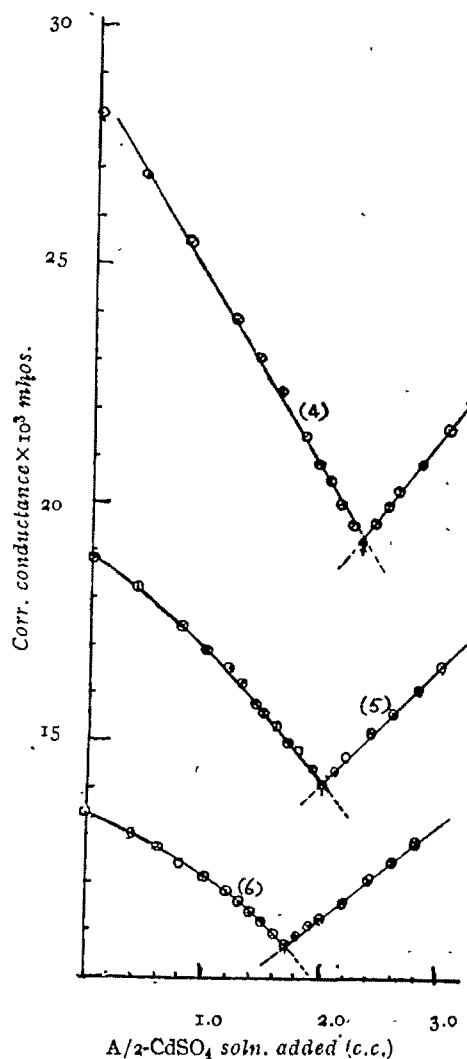


FIG. 2.



retical one required for the formation of the same compound. The effect of addition of alcohol in increasing amounts in direct titrations is to gradually decrease the observed titre values; in the reverse titrations an increase is observed under the same conditions.

The discrepancy between the observed and the theoretical titre values in aqueous medium in the case of direct and reverse titrations is due to hydrolysis of the precipitated cadmium ferrocyanide (cf. Part IV, *loc. cit.*). In the presence of increasing amounts of alcohol the hydrolysis of the compound is checked to some extent, and it is observed that the titre values approach more or less the theoretical ones in the direct and the reverse cases in the presence of 20% alcohol (by volume). The adsorption of Cd^{++} and $(\text{FeCy}_6)^{4-}$ ions by the precipitated compound from the surrounding solution also explains this discrepancy to some extent, but, as has been previously observed (*loc. cit.*), it appears that the role of hydrolysis in the precipitation of the compound is predominant.

FIG. 3.

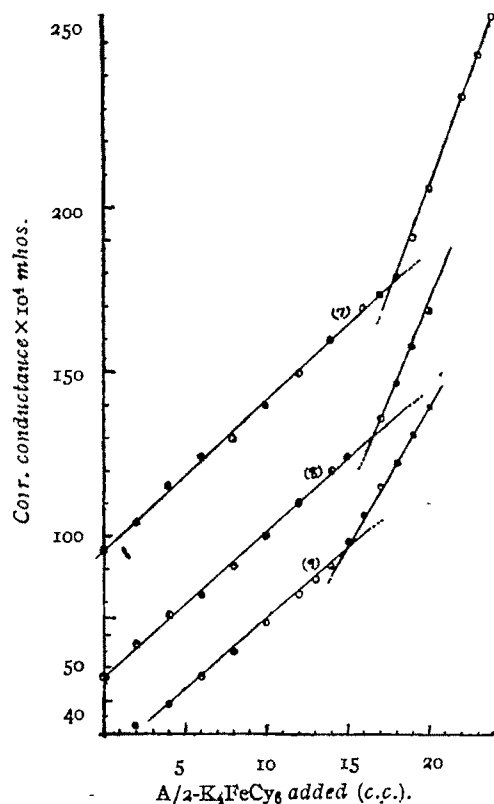
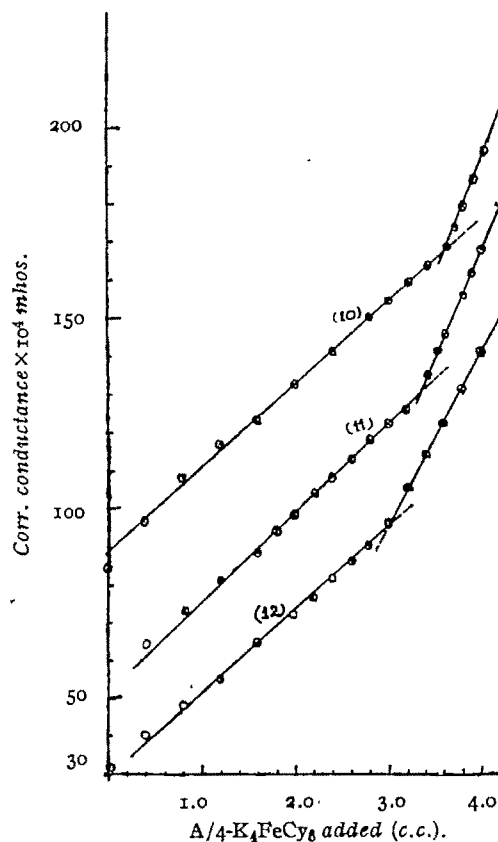


FIG. 4.



Hence the results of the thermometric, potentiometric and conductometric titrations can be correlated, and a conclusive evidence is obtained for the formation of the compound $K_2CdFeCy_2$.

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PHYSICAL CHEMISTRY LABORATORY,
AGRA COLLEGE, AGRA.

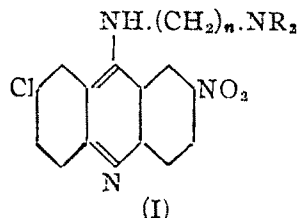
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SYNTHESES IN THE ACRIDINE SERIES. PART VI*. N-SUBSTITUTED 2-CHLORO-7-NITRO-9-AMINOACRIDINES

BY GURBAKHSH SINGH AND MAHAN SINGH

Ten N-substituted 2-chloro-7-nitro 9 aminoacridines have been prepared with a view to testing their antimalarial properties.

Magidson, Grigorowsky and Galperin (*J. Gen. Chem. Russ.*, 1938, 8, 56) have found that when the methoxy group in the 2 position in the atebirin molecule [2-methoxy-6-chloro-9-(ω -diethylaminoisoamyl)aminoacridine dihydrochloride] is substituted by a chlorine atom, the antimalarial activity is not affected. Again, Magidson and Grigorowsky (*Ber.*, 1936, 61, 396) have noticed that the antimalarial activity is considerably increased if a nitro group is introduced in the acridine nucleus at position 6 or 7, as compared to cases where no substituent is present. The improvement is more marked, if the entrant nitro group occupies the 7 position (and not the 6). A similar transfer of the chlorine atom is accompanied with a considerable decrease of the antimalarial properties (*cf.* Feldmann and Kopeliowitsch, *Arch. Pharm.*, 1935, 273, 488). It should be interesting to prepare compounds of the type (I), having a chlorine atom in position 2, augmented by the presence of a nitro group at position 7 and carrying a dialkylamino-alkyl grouping at position 9.



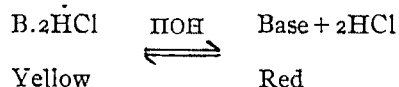
King and Work (*J. Chem Soc*, 1942, 401) found that when the sum of the carbon atoms of the N-dialkyl group in the series N-dialkylaminoethyl-6-methoxyquinolyl carbinols lay between 8 and 12, the activity was maximum. The higher and lower homologues were found to be inactive. We have therefore also substituted N-dipropyl-, N-dibutyl- or N-diamyl-amino and N-piperidino group in place of the terminal N-diethyl-amino grouping (as present in atebirin).

2-Chloro-5-nitrobenzoic acid has been condensed with *p*-chloroaniline to give 4-nitro-4'-chlorodiphenylamine-6-carboxylic acid. This was converted into 7-nitro-2:9-dichloroacridine by treatment with POCl₃. A number of 9-dialkylamino-alkylaminoacridines were prepared by condensing 7-nitro-2:9-dichloroacridine with the appropriate amine, followed by the purification of the free base by the decomposition of its soluble acetate (Method I; *cf.* D. R. P. 553,072). In the case of higher substituted 9-aminoacridines, found to be insoluble in dilute acetic acid, anhydrous potassium carbonate was added to the reaction mixture (Method II; *cf.* Burckhalter *et al.*, *J. Amer. Chem. Soc.*, 1943, 65, 2012). The yields obtained were between 40 and 60%

* Part V of this series has been published in the *Jour. Lahore Phil. Soc.*, 1946, 8, 41.

and considerable quantities of acridine were obtained as undesirable byproduct by the hydrolysis of 7-nitro-2:9-dichloroacridine. Condensation of various amines through 4-nitro-4'-chlorodiphenylamine-6-carboxyl chloride, and ring-closure of the resulting amide with phosphoryl chloride, however, gave better yields.

The various acridine bases obtained by condensation are bright red in colour, while their salts are yellow. The dihydrochlorides are moderately soluble in water, though the solubility increases in acidic medium. Some of the hydrochlorides hydrolyse in aqueous solution and the red insoluble bases are liberated. The effect is more prominent when an aqueous solution of the hydrochloride is boiled. Addition of a few drops of hydrochloric acid gives a yellow solution. This may be due to the hydrolysis of the weak hydrochloride into the free red base in aqueous solution.



Similarly when the hydrochloride solutions are treated with sodium acetate, the free bases are liberated.

EXPERIMENTAL

4-Nitro-4'-chlorodiphenylamine-6-carboxylic Acid.—2-Chloro-5-nitrobenzoic acid (10 g.) was mixed and ground well with *p*-chloroaniline (16 g.) and the mixture was heated in an oil-bath at 155°-160° for 30 minutes, with continuous trituration. The dark green sticky mass obtained was boiled with 250 c.c. of 10% hydrochloric acid and filtered hot. The insoluble residue was extracted with 1 litre of boiling 5% ammonia solution (charcoal). The sparingly soluble yellow ammonium salt was decomposed with hydrochloric acid. After drying it was crystallised from glacial acetic acid or absolute ethanol in sulphur yellow glistening needles, m. p. 283-84°, yield 86%. (cf. also Linnell, *Quart. J. Pharm. Pharmacol.*, 1942, **15**, 31, m. p. 284-85°). During this condensation a little dark green residue was always left, which was insoluble in hot ammonia solution. It appears to be the decarboxylation product of the above acid.

4-Nitro-4'-chlorodiphenylamine-6-carboxyl chloride was prepared by refluxing the above acid with PCl₅ (1:1 molecular ratio) in benzene for about 20 minutes, when a clear yellow solution was obtained. This was cooled and the yellow product separating was recrystallised from a small volume of benzene as yellow powder, m. p. 135-36°, yield 75%. (Found: N, 9.27. C₁₃H₈O₃N₂Cl₂ requires N, 9.0 per cent). No acid chloride was found when the reaction was carried in absolute petroleum ether (b. p. 40°-60°).

7-Nitro-2:9-dichloroacridine.—The above acid on treatment with phosphoryl chloride in the usual way was converted into the acridine. It was crystallised from absolute benzene in small, yellow needles, m. p. 208-09°, yield 75%. (Found: N, 9.71. C₁₃H₈O₂N₂Cl₂ requires N, 9.56 per cent). The acridine gradually hydrolysed to the corresponding acridone with evolution of hydrochloric acid gas. It was used for condensation a few hours after its crystallisation.

2-Chloro-7-nitro-9-(γ-diethylaminopropyl)aminoacridine (Method I).—A mixture of 7-nitro-2:9-dichloroacridine (3.11 g., mol.) and freshly distilled phenol (14 g.)

was warmed on a steam-bath, until solution was effected. To the hot phenolic solution was added γ -diethylaminopropylamine (1.3 g., 1 mol.). Heating was continued for another 3 hours with occasional shaking. After cooling, the reaction mixture was poured into excess of 2*N*-sodium hydroxide solution. The red base was extracted with chloroform. The chloroform extract was shaken with 5% acetic acid solution and the chloroform layer rejected. The acetate was decomposed with dilute alkali and the base taken up in chloroform (40 c. c.). After drying over potassium carbonate it was diluted with anhydrous ether (50 c. c.) and the dihydrochloride was precipitated by the addition of alcoholic hydrogen chloride as a semi-solid mass. After leaving overnight, it was crystallised from a mixture of absolute alcohol and acetone as bright yellow powder, m. p. 212-14° (d). It is soluble in water, giving an orange coloured solution, which turns yellow on the addition of a few drops of hydrochloric acid. (Found: N, 12.43. $C_{20}H_{23}O_2N_4Cl$, 2HCl requires N, 12.10 per cent).

2-Chloro-7-nitro-9-(δ -diethylaminobutyl)aminoacridine dihydrochloride was prepared by the condensation of 7-nitro-2:9-dichloroacridine and δ -diethylaminobutylamine according to Method I. It was crystallised from absolute alcohol in yellow glistening microcrystalline powder, m. p. 224-26° (d). It is moderately soluble in water. (Found: N, 12.12. $C_{21}H_{25}O_2N_4Cl$, 2HCl requires N, 11.82 per cent).

2-Chloro-7-nitro-9-(ϵ -diethylaminoamyl)aminoacridine dihydrochloride was crystallised from a mixture of absolute alcohol and acetone as a yellow powder, m. p. 235-36° (d). (Found: N, 11.05. $C_{22}H_{27}O_2N_4Cl$, 2HCl requires, N, 11.48 per cent). Considerable quantities of acridine (40%) were obtained during this reaction. Much better results were obtained through the acid chloride. 4-Nitro-4'-chlorodiphenylamine-6-carboxyl chloride (3.11 g., 1 mol.) was dissolved in 60 c. c. of dry benzene. ϵ -Diethylaminoamylamine (1.58 g., 1 mol.) was added and the mixture refluxed for 30 minutes to complete the amide formation. To effect the ring-closure, phosphoryl chloride (10 c. c.) was added and refluxing continued for another 3 hours. During this time the solid dihydrochloride of the condensation product had separated. Benzene was decanted off and the residue washed with absolute ether. It was decomposed with alkali and the red base extracted with chloroform. The dihydrochloride was precipitated as described.

*2-Chloro-7-nitro-9-(γ -di-*n*-propylaminopropyl)aminoacridine dihydrochloride* was prepared according to Method I. It was crystallised from a large volume of absolute alcohol in glistening yellow crystals, m. p. above 320° (d). The alcoholic filtrate on dilution with ether gave more of the substance, m. p. 236-38°. It appears to be a hydrate (with ether of crystallisation), as shown by a low nitrogen analysis. The anhydrous substance, as obtained by crystallisation from absolute alcohol, analysed well. (Found: N, 11.25. $C_{22}H_{27}O_2N_4Cl$, 2HCl requires N, 11.48 per cent). It is sparingly soluble in water, undergoing hydrolysis.

*2-Chloro-7-nitro-9-(γ -di-*n*-butylaminopropyl)aminoacridine* (Method II).—7-Nitro-2:9-dichloroacridine (3.11 g., 1 mol.) and phenol (12 g.) were warmed to effect solution. Anhydrous potassium carbonate (0.69 g., 1 mol.) was added and the mixture heated for 10 minutes. Di-*n*-butylaminopropylamine (1.86 g., 1 mol.) was added and the mixture heated at 100° for 3 hours. After cooling, it was added to

150 c.c. of chloroform and phenol was removed by washing with sodium hydroxide solution. After drying over anhydrous potassium carbonate, chloroform was evaporated to half its volume and 50 c.c. of ether added. Addition of alcoholic hydrogen chloride precipitated the dihydrochloride which was crystallised from absolute alcohol in yellow glistening crystals (with alcohol of crystallisation). The compound did not show a sharp melting point and could not be made anhydrous by heating at 100° in an air-oven for 15 hours. When it was crystallised from a mixture of absolute alcohol and ether (as a yellow powder), it melted above 330° with previous darkening at 270° . The analytical results were satisfactory. (Found : N, 10.74. $C_{24}H_{31}O_2N_4Cl$, 2HCl requires N, 10.86 per cent). The dihydrochloride is very sparingly soluble in water and also shows hydrolysis effect.

2-Chloro-7-nitro-9-(γ -di-n-amylaminopropyl)aminoacridine dihydrochloride was prepared according to Method II. It was crystallised from absolute alcohol in yellow crystals, m. p. above 310° (decomp.), yield 35%. A better yield (60%) was obtained through the acid chloride. It is sparingly soluble in water. (Found : N, 10.15. $C_{26}H_{36}O_2N_4Cl$, 2HCl requires N, 10.30 per cent).

2-Chloro-7-nitro-9-(γ -piperidinopropyl)aminoacridine.—The condensation was carried out according to Method I. The reaction mixture was poured into ether. The solid product obtained was collected on suction, and thoroughly washed with ether. It was then treated with excess of 5% acetic acid solution. The soluble acetate was filtered free of any insoluble acridone and then decomposed with alkali. The free acridine base was crystallised from a mixture of absolute alcohol and chloroform into ruby-red glistening slender needles, m. p. $199-200^{\circ}$. The base is soluble in dilute hydrochloric acid giving a yellow solution. (Found : N, 14.00. $C_{21}H_{23}O_2N_4Cl$ requires N, 14.05 per cent).

2-Chloro-7-nitro-9-(2'-methoxy-6'-chloro-9'-acridyl)aminoacridine.—A mixture of 7-nitro-2:9-dichloroacridine (1 g.), phenol (5 g.) and 2-methoxy-6-chloro-9-aminoacridine (0.83 g.) was heated at 100° for 4 hours. After cooling, the reaction mixture was poured into excess of dilute sodium hydroxide solution. After trituration, the red product obtained was filtered and washed with water. After drying it was crystallised from absolute alcohol in small orange-red crystals, m. p. $192-94^{\circ}$. (Found : N, 10.62. $C_{27}H_{16}O_3N_4Cl_2$ requires N, 10.87 per cent).

COMPLEMENTARY SERIES AND CONJUGATE FRAGMENTS IN URANIUM FISSION *

BY BHUPESH CHANDRA PURKAYASTHA

The fission yield values have been utilised in identifying complementary series in uranium fission. It has been concluded that the two series, whose yield values have got approximately identical positions in the yield-mass curves, are complementary to each other. From the complementary series thus identified, conjugate fragments, which are responsible for a pair of chains in question, have been sorted out. The view that a complementary series is solely due to the β -decays of a single pair of initial primary fragments has been shown to be erroneous in the light of practical experience. It has been argued that each and every nucleus in a pair of complementary series has not only a primary origin but the yield in each case is made up of the primary fission and the β -decays of the predecessors. Different probable modes of fission in between the stable members of each pairs of a complementary series, with an assumption that the sum of the charges of the two-conjugate fragments in each case is 92, has been considered. It has been argued that fission probabilities of all processes of primary formation in a pair of complementary series are not equal. The main contribution to the yield is due to one pair of conjugate fragments. The mass/charge values of this most probable pair are approximately equal. The fission frequency of the other conjugate fragments gets less and less and merges beyond the range of experimental observation as the mass/charge values of the conjugate fragments diverge from this equivalent point. The general feature of a complementary series may be pictured as follows :

$$(46-c)M(117-m) \overset{\curvearrowright}{\text{---}} \overset{\curvearrowright}{\text{---}} 92\text{U}_{236} \text{---} \overset{\curvearrowleft}{\text{---}} \overset{\curvearrowleft}{\text{---}} (46+c)M(117+m)$$

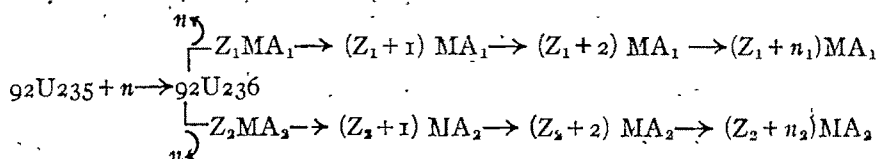
in which $(117-m)$ and $(117+m)$ stand for mass numbers of light and heavy nuclei respectively and $(46-c)$ and $(46+c)$ represent the respective charge numbers. The most probable conjugate fragments in each complementary series have been found out. From practical evidences it has been argued that in a chain at least three consecutive isobars with charge numbers either lower or higher than that of the most probable fragment may be expected. On this basis the total number of active nuclei (in between mass numbers 76 and 158) expected in fission are 549 and only 165 among these have been so far known.

As a result of rapid progress in the study of nuclear fission, 170 active isotopes of 35 elements from ^{30}Zn to ^{64}Gd have now been discovered (Plutonium Project Report, *J. Amer. Chem. Soc.*, 1946, **68**, 2411). The mass numbers of the isotopes range from 72 to 158 and indicate the presence of 87 radioactive chains. A chain is provisionally termed light when its mass number is either equal to or below 117, and heavy when its mass number lies above 117. We have 46 radioactive chains in the light group and 41 chains fall in the heavy group. It is an established fact that corresponding to a chain in the light group there is a chain in the heavy group. But the observations so far recorded from the ionisation and cloud chamber studies are such that we are confronted with a mass phenomenon involving huge number of different fission processes and as such we cannot trace the individual complementary chains and after that cannot sort out the conjugate fragments which are responsible for the complementary chains in question. The object of the present investigation is to find out the individual complementary series

* A portion of this work was published as a short note in *Science & Culture*, 1947, **13**, 255.

from an analytical study of the yield-mass curve (Fig. 1) and to sort out the conjugate fragments due to which the complementary series in question have been formed.

A typical fission process can be symbolically written as follows :—



$A_1 = 117 - m$, $A_2 = 117 + m$, $A_1 + A_2 = 234$ as shown later, m has been found to vary from 0 to 41; $Z_1 + Z_2 = 92$. $A_1 + A_2 + x = 236$, $x =$ number of neutrons released which is shown in this paper to be 2. The chain A_1 may be termed the light chain and A_2 , the heavy chain. Each primary product of fission A_1 and A_2 undergoes successive β -disintegrations till it ends in stable atoms: $(Z_1 + n_1) \text{MA}_1$ and $(Z_2 + n_2) \text{MA}_2$.

The two chains (A_1 and A_2) arising out of any one act of fission, as pictured above, may be said to be "conjugate". The two nuclei, $Z_1 \text{MA}_1$ and $Z_2 \text{MA}_2$ ($Z_1 + Z_2 = 92$), which are initially produced in a pair of conjugate chains may be termed conjugate fragments. The mass numbers A_1 and A_2 may be designated as complementary numbers. It has been shown subsequently that each of the members, namely $(Z_1 + 1) \text{MA}_1$, $(Z_1 + 2) \text{MA}_1$ etc. and $(Z_2 + 1) \text{MA}_2$, $(Z_2 + 2) \text{MA}_2$ etc. in addition to its being produced by β -disintegration of the predecessor, is also formed as a primary fragment; and conjugate nuclei like $(Z_1 + 1) \text{MA}_1$, $(Z_2 - 1) \text{MA}_2$; $(Z_1 - 1) \text{MA}_1$, $(Z_2 + 1) \text{MA}_2$ etc. may be produced. The pair of chains that we observe with complementary numbers A_1 and A_2 are then due to a number of conjugate chains as defined above, and such a pair may be termed complementary chains or series.

In Fig. 1, the logarithms of the fission yield has been plotted against mass numbers. In Table I, the fission yields have been arranged in a way and in order so that approximately identical yields with corresponding light and heavy mass numbers fall in the same columns. The data have been taken from the report of a lecture delivered by A. V. Grosse (*Chem. Eng. News*, 1947, 25, 1509).

From the yield-mass curve (Fig. 1) we note the following points:

(1) The two exactly similar and identical curves, one due to light mass numbers from 72 up to 116 and the other due to heavy mass numbers from 118 upwards up to 158, appear to meet at the point due to mass number 117. The two curves are so much exactly similar that the whole figure can be folded about the mass line 117.

(2) Both the curves rise at first steeply as we pass from lower mass number to higher mass numbers in the light group and higher to lower mass numbers in the heavy group and then in both the cases the rate of rise falls, as a result there are two humps, after which there are steep falls which are again followed by flattened portions and ultimately the two curves meet at yield point due to mass number 117.

(3) The total per cent of yield in the light series is approximately equal to that in the heavy series. (The two together are twice the per cent of fission due to which the light and the heavy nuclei have been formed).

Fig. 1

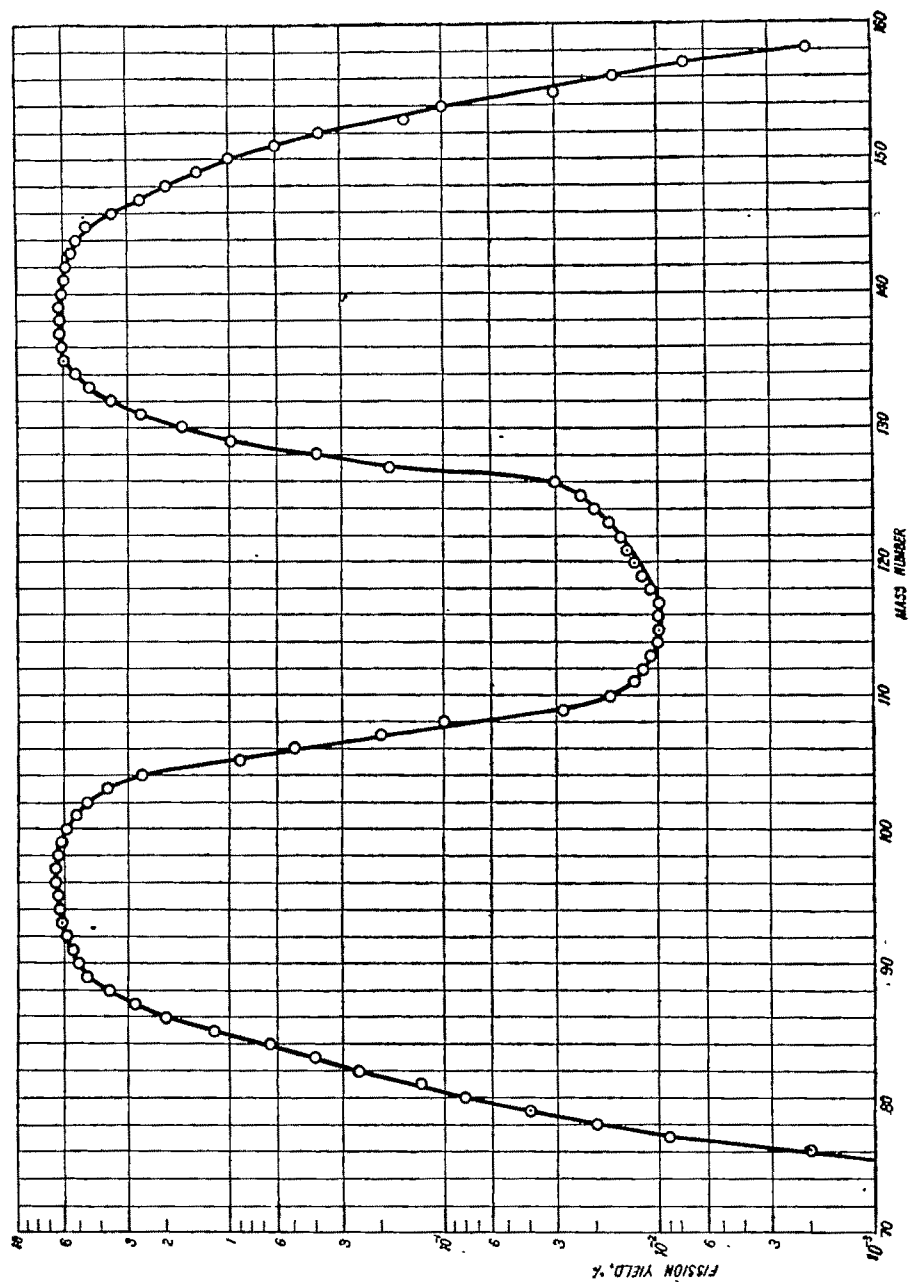


TABLE I

L i g h t		H e a v y		L i g h t		H e a v y	
Mass.	Yield.	Yield.	Mass.	Mass.	Yield.	Yield	Mass
72	1.5×10^{-5}			95	6.4	6.3	139
73	1.0×10^{-4}			96	6.6	6.3	138
74	2.0×10^{-4}			97	6.6	6.3	137
75	8.0×10^{-4}			98	6.4	6.1	136
76	2.0×10^{-3}	2.0×10^{-3}	158	99	6.2	6.0	135
77	9.1×10^{-3}	7.4×10^{-3}	157	100	5.8	5.2	134
78	2.0×10^{-2}	1.6×10^{-2}	156	101	5.2	4.5	133
79	4.0×10^{-2}	3.0×10^{-2}	155	102	4.6	3.6	132
80	8.0×10^{-2}	1.0×10^{-1}	154	103	3.7	2.6	131
81	1.3×10^{-1}	1.5×10^{-1}	153	104	2.6	1.7	130
82	2.5×10^{-1}	3.8×10^{-1}	152	105	9.0×10^{-1}	1.00	129
83	4.0×10^{-1}	6.0×10^{-1}	151	106	5.0×10^{-1}	4.0×10^{-1}	128
84	6.5×10^{-1}	1.0	150	107	2.0×10^{-1}	1.8×10^{-1}	127
85	1.2	1.4	149	108	1.0×10^{-1}	3.0×10^{-2}	126
86	2.0	2.0	148	109	2.8×10^{-2}	2.3×10^{-2}	125
87	2.8	2.6	147	110	1.7×10^{-2}	2.0×10^{-2}	124
88	3.7	3.5	146	111	1.3×10^{-2}	1.7×10^{-2}	123
89	4.6	4.6	145	112	1.21×10^{-2}	1.5×10^{-2}	122
90	5.0	5.2	144	113	1.1×10^{-2}	1.4×10^{-2}	121
91	5.4	5.5	143	114	1.0×10^{-2}	1.3×10^{-2}	120
92	5.8	5.8	142	115	1.0×10^{-2}	1.2×10^{-2}	119
93	6.1	5.9	141	116	1.0×10^{-2}	1.1×10^{-2}	118
94	6.3	6.2	140	117	1.0×10^{-2}		

(4) It is further obvious that corresponding to a light point, there is a heavy point with almost identical yield (which may be taken to be the same within experimental error), e. g., 84 and 150. We can trace such complementary numbers from 76 to 117 on the light side and corresponding ones from 158 to 117 on the heavy side. In the light series, we start with mass number 72, but no heavy mass numbers complementary to 72 and for higher numbers up to 75, have yet been found in the heavy group. This is partly due to low fission frequency of this type of fission and partly due to difficulty encountered in the separation of the rare-earths which are the most probable nuclei in this region or it may so happen that these mass numbers result from ternary fission. The mass numbers from 72 to 75 have not been shown in Fig. 1 for want of accommodation.

(5) The sum of the two mass numbers which have approximately identical positions in the yield-mass curve is always 234.

From the facts pointed out above the following conclusions can be arrived at:

(1) As far as fissions with slow neutrons are concerned, each series in the light group has a complementary series in the heavy group.

(2) Two series are complementary when their positions in the yield-mass curves are approximately identical. For instance, the series due to mass number 76 has identical yield and has position identical with that of mass number 158 and so these two are complementary. From these two extreme ends (at 76 and 158) as we pass from mass number to mass number, each pair represents units of complementary series till the point representing the series with mass number 117 from both the side is approached. This series (with mass 117) represents a case of symmetrical fission. So the general equation for series in nuclear fission will be as follows :

$$Z. M (117 - m) \xrightarrow[n\gamma]{n} {}^{92}\text{U}_{236} \xrightarrow[n\gamma]{n} Z'. M (117 + m)$$

where the values of m varies from 0 to 41 (as far as observation goes).

'How to find out the conjugate fragments' is the second aspect of this investigation. Fission nuclei form long chains of β -disintegrating series. At the first sight it seems that all the isobars in the series have been formed by successive β -disintegration of an isobar of lower nuclear charge. From this point of view, the birth of a pair of complementary series is due to the fissions of uranium nucleus into two conjugate fragments in a way so that the sum of the charges of the two nuclei is 92 ; these two primary fragments by successive β -disintegrations give rise to the complementary series in question and all other nuclei excepting these two primaries are of secondary origin.

But there are no evidences for the existence of two primary fragments. Even if we identify a series to be complementary to another by the equivalence of yield values, as suggested by us, we cannot find out the exact point of division (as regards charge) where a uranium nucleus breaks up if we are guided by the idea that a series in question has been formed only by successive β -disintegration of a single nucleus. For instance, the series which starts with ${}^{54}\text{Xe } 145$ is complementary to the series which seems to start from ${}^{36}\text{Kr } 89$ as far as yield/mass values are concerned. If we assume that ${}^{36}\text{Kr } 89$ is a primary product then ${}^{56}\text{Ba } 145$ should also be primary but ${}^{56}\text{Ba } 145$ has been shown to grow from ${}^{54}\text{Xe } 145 \rightarrow {}^{55}\text{Cs } 145 \rightarrow {}^{56}\text{Ba } 145$; similarly if ${}^{54}\text{Xe } 145$ is supposed to be a primary product, the conjugate primary fragment shall be ${}^{38}\text{Sr } 89$, but ${}^{38}\text{Sr } 89$ has been shown to grow from ${}^{36}\text{Kr } 89 \rightarrow {}^{37}\text{Rb } 89 \rightarrow {}^{38}\text{Sr } 89$. Even putting aside the idea of complementary series, if we assume that some krypton isotopes are primary, there must be at least some corresponding barium isotopes which should also be primary, but all the barium isotopes detected in fission are found to be formed by β -decay of ${}^{55}\text{Cs}$. Similarly if ${}^{54}\text{Xe}$ isotopes are supposed to be primary, the corresponding isotopes in the light group *i. e.*, isotopes of ${}^{38}\text{Sr}$ should be primary, but all the isotopes of ${}^{38}\text{Sr}$ detected in fission have been found to be formed by β -decay of the predecessors. The series headed by kryptons and xenons constitute 89% of the total fission yield (200%) but their origin cannot be explained by supposition that the existence of so many isobars in a series is only due to the successive β -decay of a single isobar of lower nuclear charge. Similarly, for instance, if we take ${}^{35}\text{Br}$ as primary in the series which have been observed to start

from ^{35}Br , we must have ^{57}La as a primary particle, but all the lanthanum isotopes observed in fission have been shown to grow from their corresponding predecessors. It should be pointed out that isobars with comparatively low nuclear charge in a series are short lived and their detections up to xenons and kryptons in the regions concerned have been only possible due to bubbling method developed by Hahn (*Naturwiss.*, 1939, **27**, 89, 163, 529). It seems that all other series can also be extended to isobars of lower nuclear charge provided experimental technique facilitating their detections is developed.

In addition to evidences set forth above it has been observed (Plutonium Project Report, *loc. cit.*) that in a series an isobar with lower nuclear charge has an yield lower than that of an isobar with higher nuclear charge (Table II) and that in some cases a β -active nucleus of low fission yield with a nuclear charge higher than that of a stable member of the series has also been discovered (*cf.* Table III).

TABLE II

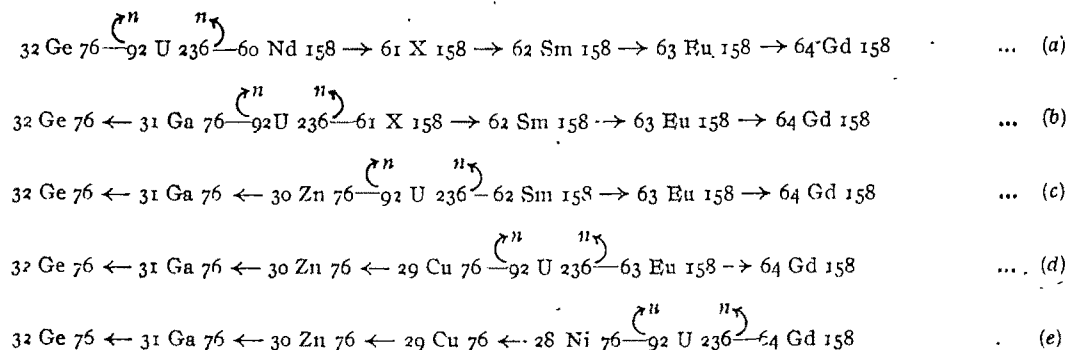
Mass No.	Nuclei.	Yield %.	Mass No.	Nuclei.	Yield %.
77	$^{32}\text{Ge } 77$ ↓ $^{33}\text{As } 77$	0.0037 0.0091	83	$^{34}\text{Se } 83$ ↓ $^{35}\text{Br } 83$	0.21 0.41 0.31
Mass No.	Nuclei.	Yield %	Mass No.	Nuclei.	Yield %.
91	$^{38}\text{Sr } 91$ ↓ $^{39}\text{Y } 91$	5.0 5.9	135	$^{53}\text{I } 135$ ↓ $^{54}\text{Xe } 135$	5.6 5.9
			141	$^{56}\text{Ba } 141$ ↓ $^{57}\text{La } 141$ ↓ $^{58}\text{Ce } 141$	4.6 5.7

TABLE III

Stable isobar in a series with lower nuclear charge.		β -Active isobar with higher nuclear charge.			Expected conjugate fragments in the complementary series.
Nuclei.	Series yield%.	Nuclei.	Half life.	Yield %.	
$^{34}\text{Se } 82$	2.5×10^{-1}	$^{35}\text{Br } 82$	34 hrs.	2.8×10^{-5}	$^{57}\text{La } 152$
$^{36}\text{Kr } 86$	2.0	$^{37}\text{Rb } 86$	19.5 days	1.6×10^{-4}	$^{55}\text{Cs } 148$
$^{54}\text{Xe } 136$	6.1	$^{55}\text{Cs } 136$	13.0 days	0.01	$^{37}\text{Rb } 136$

From the observations as stated above it is clear that the view that a uranium nucleus breaks up solely into two primary fragments and these two primaries by successive β -disintegrations give rise to a complementary series and that all other nuclei excepting a single primary in a series are solely secondary, is absolutely wrong. On the other hand, these observations seem to suggest that possibly each isobar in a series is derived from both primary and secondary origins. As for instance, the products with mass number 76 and that with 158 have got identical yield and as such are complementary to each other in fission. All possible modes of fission including stable members of both the groups are represented below (Scheme 1).

SCHEME I

Conjugate chains in a complementary series.

It appears from the above equations that all expected nuclei excluding ${}^{60}_{\text{Nd}}158$ and ${}^{28}_{\text{Ni}}76$ (which are regarded provisionally to be primaries) are primary and secondary at the same time and that a nucleus, e.g. stable ${}^{32}_{\text{Ge}}76$ can originate as a primary fragment in a fission process as given at the head of the figure, but also as a secondary product in a number of ways as illustrated above. The complementary series mentioned above are due to at least five distinct modes of fission of uranium nuclei. Question naturally arises "Do the five pairs of conjugate fragments, as pictured above, contribute equally to the yield of the complementary chain?" The yield values in Tables II and III give a strong indication that each distinct mode of fission into conjugate fragments cannot have equal frequency, and suggest that the main contribution to the yield is due to one pair of conjugate fragments. It has been supposed that the mass/charge ratio values of this particular pair of conjugate fragments are approximately equal and frequency of the other conjugate fragments becomes less and less as the mass/charge ratio values diverge from this equivalent point. In Table IV are given the values of mass/charge ratios of the conjugate fragments as pictured in Scheme I. In the calculation, one unit of mass in each case has been added to the complementary numbers in consideration of the fact that each one of the conjugate fragment releases one neutron just after fission

TABLE IV

Eq. No.	76 L i g h t		158 H e a v y	
	A/Z_1	Values	A_1/Z_1	Values.
(a)	77/32	2 406	159/60	2 650
(b)	77/31	2 484	159/61	2 607
(c)	77/30	2 566	159/62	2 564
(d)	77/29	2 656	159/63	2 524
(e)	77/28	2 250	159/64	2 484

From the values it seems that the frequency is maximum due to equation (c), and as the values of mass/charge ratio of the conjugate fragments diverge from the equivalent point, the corresponding frequency of fission may be supposed to become less and less

till at last the frequency of the conjugate nuclei becomes so small that their yield goes beyond the limit of experimental observations.

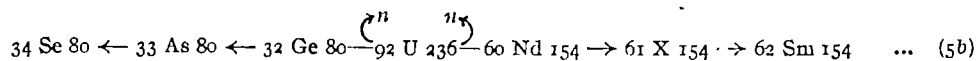
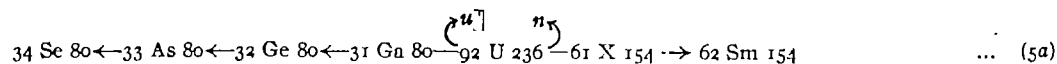
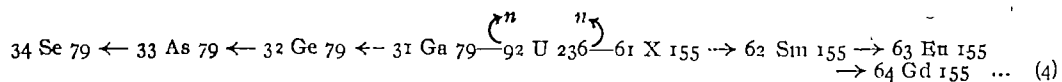
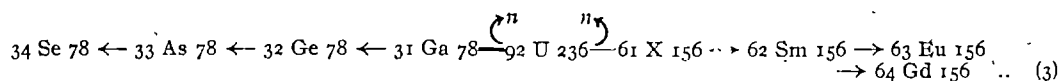
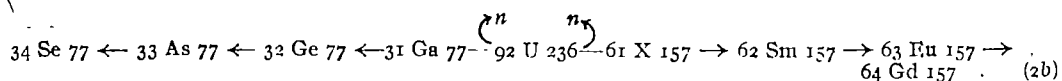
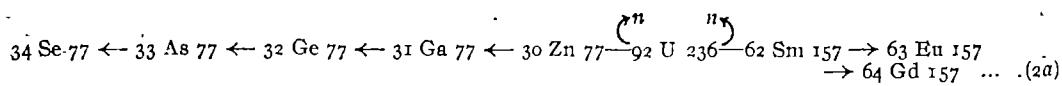
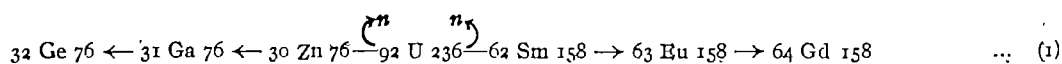
From such considerations, as stated above, the most probable charge numbers in each complementary series have been found out. The symmetrical fission has been found to be symmetrical both as regards mass and charge as far as the series with maximum yield is concerned. Hence, a general equation for fission both as regards mass and charge can be written as follows.

$$(46-c) M (117-m) \xrightarrow{n} {}_{92}U_{236} \xrightarrow{n} (46+c) M (117+m)$$

where the value of c for the most probable charge numbers varies from 0 to 16.

SCHEME 2

Most probable conjugate chains in a few complementary series.



DISCUSSION

Most Probable Charge Numbers

From what has been said before it appears that there must be a most probable pair of conjugate fragments in a complementary series. Being guided by the ideas that there is a uniform distribution of neutrons and protons in most of the nuclei undergoing fission (Davidson and Watson, *Phys. Rev.*, 1947, **71**, 742) we have assumed that the mass/charge ratio values of the most probable pair are equal. In calculations the values which do not differ by more than 1% have been taken to be equivalent. In some complementary series it has been found that the ratio values differ by near about 3%, and that there is another pair of consecutive conjugate fragments with approximately identical divergence,

as: 96/38, 2.526; 140/54, 2.592; and 96/37, 2.595; 140/55, 2.545. In such cases it has been assumed that there are equal probability of contributions by both the pairs. On this basis, a list of equations denoting complementary series corresponding to maximum yield has been derived. A portion of the list has been inserted in Scheme 2.

It will be evident from Scheme 2 that the same element, characterised by a definite charge number, can at best be the most probable fragment in four complementary series. It is further obvious that in case of equal probability of contributions by two pairs of conjugate fragments, the same mass number is found to have two charge numbers as most probable fragments. The most probable conjugate charge numbers with their corresponding mass numbers and the yield of the most probable charge numbers are given in Table V. As the yield of a complementary series is mainly due to the most probable conjugate fragments, so, as a first approximation, the series yield has been assumed to correspond to the yield of the most probable charge number in question. It has already been stated that in some series two charge numbers appear as most probable fragments. In such cases, half of the series yield has been attributed to each charge number. As an illustration let us take a most probable charge number, say 35. From Table V we note that element 35 appears as a most probable fragment for mass numbers 87, 88, 89 and 90. For mass number 87 it shares the yield values with charge number 34, whilst for mass number 90 it shares with charge number 36. So the yield value of charge number 35

$$= \frac{\text{yield (87)}}{2} + \text{yield (88)} + \text{yield (89)} + \frac{\text{yield (90)}}{2}.$$

In this way the yield values of most probable conjugate charge numbers have been found out and inserted in Table V. In the table the mass numbers which relate to one most probable fragment have been shown in *italics*.

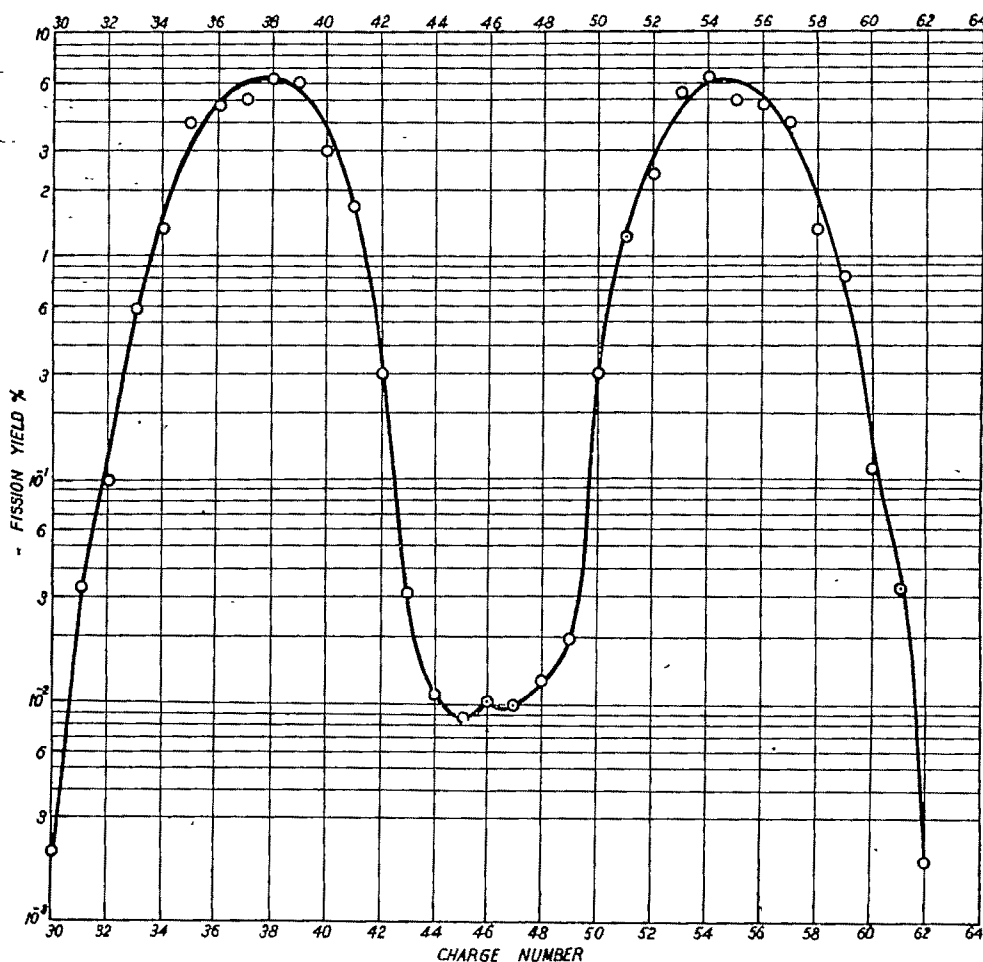
TABLE V

Most probable charge No.	Light		Heavy		Most probable charge No.
	Mass No.	Yield %.	Yield %.	Mass No.	
30	76, 77	6.06×10^{-1}	5.7×10^{-1}	158, 157	62
31	77, 78, 79, 80	1.00×10^{-1}	0.997×10^{-1}	157, 156, 155, 154	61
32	80, 81, 82	3.00×10^{-1}	3.9×10^{-1}	154, 153, 152	60
33	82, 83, 84, 85	1.78	2.49	152, 151, 150, 149	59
34	85, 86, 87	4.00	4.00	149, 148, 147	58
35	87, 88, 89, 90	12.2	12.0	147, 146, 145, 144	57
36	90, 91, 92, 93	13.85	13.95	144, 143, 142, 141	56
37	92, 93, 94, 95	15.45	15.15	142, 141, 140, 139	55
38	95, 96, 97, 98	19.06	18.80	139, 138, 137, 136	54
39	98, 99, 100, 101	17.8	16.55	136, 135, 134, 133	53
40	101, 102, 103	9.05	7.20	133, 132, 131	52
41	103, 104, 105, 106	5.15	3.70	131, 130, 129, 128	51
42	105, 106, 107, 108	9.5×10^{-1}	9.0×10^{-1}	129, 128, 127, 126	50
43	108, 109, 110, 111	9.3×10^{-2}	6.0×10^{-2}	126, 125, 124, 123	49
44	110, 111, 112, 113	3.25×10^{-2}	3.95×10^{-2}	124, 123, 122, 121	48
45	113, 114, 115, 116	2.55×10^{-2}	3.15×10^{-2}	121, 120, 119, 118	47
46	115, 116, 117	1.5×10^{-2}	1.65×10^{-2}	119, 118, 117	46

In Fig 2, 1/3 of the fission yield% has been plotted against charge numbers.

In Fig. 2, the logarithms of the yields values of the most probable charge numbers have been plotted against charge numbers. The curve is exactly the same as mass *versus* yield curve (Fig. 1). The most probable conjugate charge numbers have nearly equal yield and approximately identical position in the curve.

Fig. 2



Predictions

Long chains of β -disintegrating chains are observed in fission. It has been stated that in a series the yield is due to most probable charge number, so in a chain an isobar with a nuclear charge lower than that of the most probable fragment will have very small yield, while in the case of an isobar with a nuclear charge higher than that of the most probable fragment, the yield will be enhanced by the β -decay of the most probable fragment. From such considerations we note that the most probable charge numbers divide the active isobars in a series into two groups, namely, isobars with nuclear charges lower

than that of the most probable fragment and isobars with nuclear charges higher than that of the most probable fragment.

Out of the 83 chains from mass numbers 76 to 158, there are only 20 chains in which isobars beginning from stable members up to the most probable fragments have been discovered. The total number of β -active nuclei from the stable members up to most probable fragments in the 83 chains are 273. Of these only 144 nuclei have so far been discovered. We can therefore expect 129 β -active nuclei in this region.

There are, however, some series, say series with mass number 145, $^{145}_{54}\text{Xe} \rightarrow ^{145}_{55}\text{Cs} \rightarrow ^{145}_{56}\text{Ba} \rightarrow ^{145}_{57}\text{La} \rightarrow ^{145}_{58}\text{Ce} \rightarrow ^{145}_{59}\text{Pr} \rightarrow ^{145}_{60}\text{Nd}$ in which the most probable fragment is $^{145}_{57}\text{La}$, but the series has been traced up to $^{145}_{54}\text{Xe}$. Though the yields of nuclei with charge numbers lower than that of the most probable fragment is very low and the life periods are very short, yet we can expect three nuclei per series in the 83 chains mentioned above, provided the experimental technique to identify them is developed. On this basis the probable number of nuclei with charge number lower than those the most probable fragments is 249; but only 18 amongst them have so far been known. Therefore the number of nuclei with nuclear charges lower than those of the most probable fragments still to be discovered is 231.

From similar considerations, as stated above, a fragment with a charge number higher at least by three units than that of the most probable fragment can also be detected. Most of such nuclei fall in between most probable fragments and stable members, and number of such nuclei has already been mentioned. But on counting the isobars in series up to three units of charge higher than those of the most probable fragment, we meet with some series where there are active nuclei with charge numbers higher than those of the stable members (vide Table III). The number of expected nuclei in this region is only 27 of which three have already been detected in fission. So the number of expected active nuclei in this region is 24 and some of these may be β^+ active.

From what has been said it can be inferred that the total number of active nuclei (in between mass numbers 76 and 158) expected in fission is 549 and only 165 among them are known. On this basis the number of nuclei awaiting discovery is 384. So we note that more than $\frac{2}{3}$ of the expected active nuclei in fission have not yet been discovered.

It should be stated that the series with mass numbers 72 to 75, though observed in fission, have not been the subject matter of our discussions. This is because there is no evidence of any heavy chain corresponding to any one of them. The absence of any heavy chain may be either due to low fission frequency and difficulties in the separation of the rare-earths which are most probable fragments here or it may so happen that these mass numbers may be derived from ternary fission, a phenomenon which cannot have any relation with the complementary series.

It should be pointed out that in a few cases, as will be evidenced from Table I and Fig. 1, that in order to generalise the fission mechanism, some allowance has been granted to error in yield determinations. The probable percentage of error with experimental details are not yet published. Specially in the heavy group, from mass numbers 130 to 134, the low values in yields against corresponding values for the light series are significant. It should be mentioned that the total yield in the light group is 100.3%,

whereas in the heavy group, as the figures stand, it is 94.8%. This 5% loss in the heavy group can reasonably be assumed to be due to error in yield values in mass numbers 130-134.

The above treatments as regards detecting complementary series is rather free from adverse criticism and the hypothesis as regards the most probable conjugate charge numbers is based on inferences from experimental observation but that the mass/charge ratio values of the most probable conjugate fragments are equal, is however, an assumption. This from a chemist's point of view is a subject experimental verification of which requires determination of the yield values of a chain with different β -disintegrating charge numbers. However, predictions that have been made, open up a wide scope of investigation in this line.

In conclusion the author expresses his deep sense of gratitude to Prof. M. N. Saha, F.R.S., for his keen interest and encouragement in the work and to Prof. P. Rây, F.N.I., for valuable criticism and discussions. The author is also indebted to Krishnapan Charity Fund for an endowment.

INSTITUTE OF NUCLEAR PHYSICS,
CALCUTTA UNIVERSITY.

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PASSIVITY OF MAGNESIUM

BY G. RAMARAO

Magnesium exhibits passivity when exposed to atmosphere in the presence of ultra-violet radiations. The extent of passivity is measured by the displacement of copper from a solution of copper sulphate. A slow current of dry air does not passivate the metal, but a rapid current activates it in the dark and passivates it on irradiation. Ionised air, produced by vigorous bubbling through concentrated sulphuric acid and passed over P_2O_5 , passivates the metal, while pure dry hydrogen, similarly ionised, activates the metal under the influence of ultraviolet radiations.

Air from a gas holder was dried by passing through a wash bottle containing concentrated sulphuric acid and then through calcium chloride towers. The dried air was passed through a silica test tube and then through an ordinary test tube which was well wrapped with a piece of black paper. The source of ultraviolet rays was an iron arc provided with a clock-work mechanism for feeding the electrodes operating at a pressure of 100 volts. A silica trough through which cold water was kept constantly circulating was placed between the arc and the silica test tube to cut off the heat of the arc.

About 25 cm. length of magnesium ribbon was well polished with fine emery paper and then well cleaned with a filter paper. Two equal lengths of 10 cm. each were cut from the ribbon, folded into loops and were inserted into the silica and glass test tubes. The silica test tube was exposed to the ultraviolet light for 30 minutes. The ribbons were then dropped into two separate conical flasks each containing 25 c.c. of copper sulphate solution. The magnesium was allowed to remain in the solution for exactly 5 minutes (the reaction ceased after 3 minutes) after which it was removed by hooked glass rod and 10 c.c. of the solution were titrated with standard thiosulphate solution.

The following table gives readings at different rates of flow.

TABLE I

(In a blank experiment 10 c.c. of $CuSO_4$ soln. required 20.4 c.c. of thio soln.)

No.	Volume of air (in c.c./min.).	Thio needed for test tube exposed to light	to dark.	Remarks
1	0	18 c.c.	18 c.c.	No effect
2	16.7	18	18
3	23.3	18	18
4	33.3	18	18
5	100	18	18
6	240	18	18
7	600	18.2	17.9	Passivated in the light, slightly activated in dark.
8	700	18.35	17.9	Passivity increases.
9	900	18.50	17.9	Passivity further increases

The following conclusions are drawn from the above observations :

- (i) For moderate rates of flow of air there is no effect of irradiation.
- (ii) A rapid stream of air passivates the metal in light.
- (iii) A rapid stream of air slightly activates the metal.

Gases ionise when vigorously bubbled through concentrated sulphuric acid and certain electrolytes ; the ionisation is further increased by drying the gas over P_2O_5 . Air was bubbled through concentrated sulphuric acid at the rate of 100 c.c. per minute and was further passed over two drying towers containing P_2O_5 and was irradiated as in the previous experiment for 30 minutes. 18.6 C.c. of thiosulphate solution were required showing that the metal was highly passivated.

The effect of irradiation in a stream of pure, dry and ionised hydrogen was next tried. Hydrogen from a Kipp was bubbled through wash bottles containing lead acetate solution and silver nitrate solution and then through P_2O_5 towers. For moderate rate of flow, volume of thio was 17.1 c.c. and at 100 c.c. of gas per minute, the volume of thio was 16.8 c.c.

C O N C L U S I O N

A current of air rapidly bubbled through concentrated sulphuric acid and dried over calcium chloride has fewer chances of drying when compared with a slow stream of air, and the moisture, thus carried with the air under the influence of ultraviolet rays, produces an-oxide film which makes the surface passive. The same rapid current of air in the dark sweeps off partly any film on the surface and slightly activates. Further, ionised air increases the passivity confirming the formation of an oxide film on the irradiated surface of the metal which becomes electro-positive. Similarly, the activation of the metal, when ionised hydrogen is passed over the electro-positive surface of the metal, proves the reduction of the oxide film. These experiments therefore support the oxide film theory of passivity.

OSMANIA TECHNICAL COLLEGE,
HYDERABAD, DECCAN.

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OXYGEN CAPACITY OF BLOOD DETERMINED BY COPPER SULPHATE METHOD

By R. J. LOKRE

Blood samples of 25 apparently normal young healthy men were examined for their oxygen capacity by the specific gravity method. The average is 21.191 c.c. which is a little less than the average of 21.62 obtained by the author.

Phillips, Van Slyke and their co-workers ("Copper sulphate method of determining specific gravity of whole blood and blood plasma") give the following equation for finding out the oxygen capacity, where Ht stands for Haematocrit value, G_b and G_p for the specific gravities of whole blood and plasma respectively,

$$\text{Oxygen capacity} = \frac{(G_b - G_p)}{1.097 - G_p} \cdot \text{Ht}$$

The technique consists of dropping drops of whole blood and plasma into graded series of copper sulphate solutions of known specific gravities ranging from 1.008 to 1.076 and differing from one another by 0.004. Each drop in entering the solution becomes enclosed in a sac of copper proteinate and remains as a discrete drop with its specific gravity unchanged for 15 to 20 seconds. The size of the drop need not be constant as the temperature coefficient of expansion of copper sulphate solution is nearly the same as that of the whole blood or plasma. No temperature correction need be applied.

The drops are allowed to fall from a height of 1 cm. from above the surface of the copper sulphate solution. If the drop is heavier, it will continue to fall even after it has lost its momentum due to fall. If it is lighter, it will rise to the surface, and will remain stationary for a few seconds if it has got the same specific gravity as that of the copper sulphate solution. When the drop is dropped care should be taken to avoid air bubbles and the formation of films on the surface of the copper sulphate solution.

The copper sulphate solutions were prepared according to the method given by the authors in their original paper. Additional care was, however, taken to determine the specific gravity of the stock solution by pipetting out 25 c.c. of the solution and determining its specific gravity by weighing it on an analytical balance. From this stock solution, the various other solutions of different specific gravities were prepared by diluting with distilled water.

For our work, we chose 25 apparently normal healthy young male students of the King Edward Medical School, Indore, varying in age between 18 and 28 years. Blood (10 c.c.) was drawn from the vein in specially prepared oxalated bulbs containing 2 mg. of neutral potassium oxalate per c.c. of blood. Within half an hour of taking the blood, the specific gravity of the whole blood was found out. The plasma was separated by centrifuging the blood and within an hour of taking the blood, its specific gravity also was determined. The values of the specific gravity of the whole blood and plasma

were corrected for the oxalate by subtracting 0.004 for each mg. of oxalate present per ml. of blood and the corrected values were used in obtaining the results.

Assuming the haematocrit value to be 46.16, an average arrived in our previous work (Gokhale and Lokre, *Ind. Med. Gaz.*, 1947, 82, No. 9) and then substituting the values of G_b and G_p , the values for the oxygen capacity were calculated. The values obtained are indicated in Table I.

In their original work, the authors of the paper claim the accuracy of this method as compared with the chemical method of Van Slyke to be within a percentage deviation of 0.88.

TABLE I

Sample No.	Oxygen.	Sample No.	Oxygen.
1	21.40 c.c.	13	18.29 c.c.
2	20.15	14	20.05
3	21.40	15	23.34
4	21.40	16	20.79
5	20.66	17	20.66
6	21.38	18	20.79
7	20.40	19	20.79
8	21.40	20	22.24
9	20.79	21	21.24
10	22.34	22	22.24
11	20.79	23	21.40
12	20.06	24	21.38
...	25	21.40
Average 21.191 c.c.			

KING EDWARD HOSPITAL LABORATORY,
INDORE

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PYRIDINE COMPLEXES OF METALLIC PERCHLORATES. PART III.
COMPOSITION AND STABILITY OF COPPER PYRIDINE
PERCHLORATES IN AQUEOUS SOLUTION

By P. C. SINHA AND R. C. RAY

An attempt has been made to determine the nature and stability of the complexes, which are formed when an aqueous solution of copper perchlorate is treated with pyridine, by measurement of the distribution coefficients of varying quantities of pyridine between benzene and a *N*/10-aqueous solution of copper perchlorate. The results seem to indicate that only two complexes are formed containing respectively 2 and 4 molecules of pyridine per atom of copper

The preparation and general properties of pyridine complexes of some metallic perchlorates have been described in a previous paper (*J. Indian Chem. Soc.*, 1943, 20, 33). From measurements of dissociation pressures of copper pyridine perchlorates at different temperatures and isothermals (pressure-composition curves at definite temperatures) it has been found that in the solid phase only two complexes, *e.g.*, $\text{CuPy}_4(\text{ClO}_4)_2$ and $\text{CuPy}_2(\text{ClO}_4)_2$ exist. It is well known that amines of anhydrous salts vary considerably in stability, and may be roughly divided into two classes, *viz.*, (a) those stable in aqueous solution and (b) those decomposed by water. It was therefore considered worthwhile to investigate the nature of the complexes formed by metallic perchlorates with pyridine in aqueous solution.

By using the spectrophotometric method Job (*Ann. chim.*, 1928, *x*, 9, 185) determined the nature of the complexes which copper sulphate formed with ammonia and ethylenediamine and found that both these bases formed complexes containing four molecules of the base per one atom of copper of the type of Schweitzer's salt. With the help of the same method Aumèras and Tamisier (*Bull. Soc. chim.*, 1933, 53, 102) studied the complex formation between copper nitrate and methylamine, allylamine, pyridine and other nitrogenous organic bases. They found that pyridine gave with copper nitrate a complex analogous to that formed with ammonia, but much more dissociated. The complex is no doubt formed through the nitrogen atom, but the work of Aumèras and Tamisier (*loc. cit.*) shows that although the nitrogen of the pyridine nucleus reacts, the nitrogen of the pentagonal nucleus is inactive with respect to the copper salt.

One way of determining the complexity of a solute in an aqueous solution is by means of the partition coefficient method. According to Nernst's distribution law, the concentration of a substance in two immiscible solvents, in equilibrium, bears a constant ratio to each other provided the molecular weight is the same in both the solvents; or, inverting the law, any deviation from the constant concentration ratio will serve as a measure of any molecular change which the distributing substance undergoes in the different solvents as pointed out by Hantz and Sebaldt (*Z. physikal. Chem.*, 1899, 30, 258). Dawson and McCrae (*J. Chem. Soc.*, 1900, 77, 1239) as also Tamisier (*Bull. Soc. chim.*, 1933, 53, 157) have utilized these facts for investigating the nature of the amines of copper, zinc and cadmium, using water and chloroform as two immiscible liquids.

In the present investigations, water and benzene have been chosen as the immiscible solvents, since chloroform is much more volatile than benzene at the temperature of the experiments. The working temperature was selected to be 35°, as the temperature of the laboratory was above 30° for major part of the year. Hantz and Sebaldt (*loc. cit.*)

have shown that the ratio of the concentrations of pyridine in benzene and water for different concentrations of pyridine is constant and independent of the initial concentration of pyridine; thus it can be safely concluded that the molecular complexity of pyridine in benzene and water is the same.

EXPERIMENTAL

Aqueous solution of the salt was prepared by taking a known volume (2.5 c.c.) of 2 *N*-copper perchlorate solution and to this varying volumes of 2*N*-pyridine solution were added. The mixture was made up to 50 c.c. with water so that the solution was *N*/10 with respect to copper perchlorate. These solutions were then poured into a number of glass-stoppered separating funnels which had been tested free from leakage. Benzene (50 c.c.) was added to each and the funnels were shaken in a thermostat maintained at $35^{\circ} \pm 0.01^{\circ}$ until equilibrium was established. The aqueous and benzene layers were allowed to separate in the thermostat and the layers were withdrawn quickly. The pyridine content of each layer was estimated separately. For the estimation of pyridine in the benzene layer, 40 c.c. of the liquid were taken in a glass-stoppered bottle, a drop of methyl orange and about 50 c.c. of water added, and the pyridine titrated with *N*-HCl until a permanent pink colour was obtained. For the estimation of pyridine in the aqueous layer, 40 c.c. of the solution was transferred to a round-bottomed flask, fitted with a rubber stopper having two holes, one of which carried a tube connected with a boiler for steam and to the other was attached an alkali trap and a condenser. Excess of concentrated sodium hydroxide solution was added to the flask and the whole of the pyridine was distilled into a bottle containing 25 c.c. of *N*-acid solution. The excess of the acid in the bottle was then titrated with seminormal sodium hydroxide solution. The results obtained are given in Table I.

TABLE I

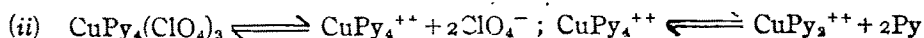
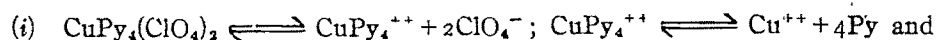
Mol. ratio $\text{Cu}(\text{ClO}_4)_2$: total pyridine.	Distribution coeff of Py in water/ Py. in benzene.	*Conc. of pyridine in benzene.	*Total conc. of pyridine in water.	*Conc. of "free" pyridine.	*Conc. of "com- bined" pyridine	No. of mols. of pyridine com- bined per atom of copper.	$K_1 \times 10^4$.	$K_2 \times 10^3$
(a)	(d)	(b)	(w)	(f)	(e)	(r)
1:10	0.639	0.3050	0.1950	0.1046	0.0904	1.808	1.45	...
1:12	0.628	0.3686	0.2314	0.1264	0.1050	2.100	2.31	30.4
1:14	0.610	0.4348	0.2652	0.1491	0.1161	2.322	3.57	11.2
1:15	0.603	0.4679	0.2821	0.1604	0.1217	2.435	4.26	9.3
1:16	0.594	0.5018	0.2482	0.1721	0.1261	2.522	5.14	8.4
1:17	0.591	0.5342	0.3158	0.1832	0.1326	2.652	5.73	6.9
1:18	0.585	0.5672	0.3328	0.1945	0.1383	2.766	6.39	6.1
1:20	0.579	0.6323	0.3677	0.2169	0.1508	3.016	7.22	4.6
1:22	0.568	0.7015	0.3985	0.2406	0.1579	3.158	8.94	4.2
1:24	0.560	0.7693	0.4307	0.2638	0.1669	3.338	9.60	3.4
1:26	0.550	0.8377	0.4623	0.2874	0.1749	3.498	9.78	2.6
1:28	0.543	0.9082	0.4918	0.3116	0.1802	3.604	10.35	2.4
1:30	0.535	0.9793	0.5207	0.3359	0.1848	3.696	10.48	2.0

* in g mol./litre

DISCUSSION

The values in column (a) are calculated from the quantities of copper perchlorate and pyridine actually present in the solutions. The distribution coefficient values are obtained by plotting the results of Hantz and Sebaldt (*loc. cit.*) and the values for 35° are determined from the curve. The figures in columns (b) and (w) are obtained from the results of experiments. From a knowledge of the distribution coefficient in pure water and benzene, it is possible to calculate the concentration of pyridine in aqueous solution which is in equilibrium with any particular concentration of pyridine in benzene. This quantity may be regarded as "free" pyridine shown in column (f). The difference between the total pyridine (w) and the "free" pyridine (f) gives the amount of pyridine which is in combination of the copper salt and these values are tabulated in column (c). Hence, it is possible to calculate the number of molecules of pyridine which is in combination with one atom of copper in the salt solution and these values are shown in column (r).

The calculation of equilibrium constants K_1 and K_2 depends upon the application of the law of mass action. This law can be applied only when the constitution of the complexes formed in the solution phase is known. As it is precisely the question of determining this constitution, which is under consideration, it is necessary to make *a priori* assumptions regarding the complexes formed and to retain those which correspond to the experimental results. Dawson and McCrae (*loc. cit.*) have found that the tetrammine complex of copper dissociates into the diammine complex. As pyridine complexes are analogous to the amines, it may be assumed that the highest pyridine complex formed in solution is the tetrapyridine complex which may dissociate in either of the two ways shown below:—



where Py stands for a molecule of pyridine, $\text{C}_5\text{H}_5\text{N}$.

On the basis of the above hypothesis,

$$K_1 = \frac{[\text{Cu}^{++}][\text{Py}]^4}{[\text{CuPy}_4^{++}]} \text{ and } K_2 = \frac{[\text{CuPy}_2^{++}][\text{Py}]^2}{[\text{CuPy}_4^{++}]}$$

If r is the number of molecules of pyridine which are in combination with an atom of copper, it can be shown that

$$K_1 = \frac{4-r}{r} [\text{Py}]^4 \text{ and } K_2 = \frac{4-r}{r-2} [\text{Py}]^2$$

The average value for K_1 obtained for copper perchlorate and pyridine is 6.5×10^{-4} which is of the same order as the value 3.1×10^{-4} found by Auméras and Tamisier (*loc. cit.*) for copper nitrate and pyridine.

The divergence in the values of K_1 and K_2 is not surprising, because the co-ordination number of a metal, like copper, is not necessarily invariable on account of the fact that in solution more than one complex are in a state of mobile equilibrium. The invariability of the co-ordination number can be considered as a result of the chemical

forces and the nature of the atoms taking part in the formation of the complex. It is not the case with copper perchlorate solution which can only form complexes by means of very mobile equilibrium corresponding to the maximum stability of the dissolved systems. It is therefore probable that a pyridine solution of copper perchlorate in water contains several complexes capable of formation according to Werner's theory, these complexes being in equilibrium with one another. When the concentrations of pyridine are changed, however, it is possible to arrive at zones of concentration where one of the complexes exists alone to the exclusion of the other, or, at least formed in the greatest proportion in comparison with the others.

Two such zones become apparent when one examines the values of τ , the number of molecules of pyridine in combination with an atom of copper. It appears that a higher and a lower pyridinated complexes are present in the solutions in mobile equilibrium with one another. The regular and steady increase and decrease respectively in the values of K_1 and K_2 seem to indicate that the higher pyridinated complex in solution dissociates progressively and rapidly into the lower pyridinated complex with the decrease in the concentration of pyridine in solution, or, in other words, the higher pyridinated complex is stable in solution only when a large excess of pyridine is present, but at low concentrations of pyridine the lower pyridinated complex is more stable. It can therefore be deduced from the results of the experiments that, in the interval of the concentrations of pyridine studied, the aqueous solution of copper perchlorate does not form several complexes but only two which contain 2 and 4 molecules of pyridine per atom of copper, especially in view of the fact that these are the complexes which exist in the solid phase.

CHEMICAL LABORATORY,
SCIENCE COLLEGE, PATNA.

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DERIVATIVES OF PHOSPHANILIC ACID

By N. S. LIMAYE AND B. V. BHIDE

Several derivatives of phosphanilic acid have been prepared

The present paper describes the synthesis of several derivatives of phosphanilic acid which resemble the derivatives of arsanilic acid and sulphanilamide possessing equivalent to or greater activity than that of the parent compound.

Phosphanilic acid (required for the purpose) was prepared following essentially the method of Bauer (*J. Amer. Chem. Soc.*, 1941, **63** 2137). *p*-Bromophenylphosphinic acid (Davies and Mann, *J. Chem. Soc.*, 1944, 276) was used instead of *p*-chlorophenylphosphinic acid as in the method of Bauer (*loc cit.*). The advantage of using *p*-bromophenylphosphinic acid is that the reaction with ammonia need not be carried out under pressure. It also gives better yields and hence is more suitable for the preparation of large quantities of phosphanilic acid.

Acetyl, butyryl, caproyl and succinyl derivatives of phosphanilic acid were prepared by shaking a solution of the acid in sodium bicarbonate with the appropriate anhydride, as the corresponding acid chlorides failed to react in the presence of pyridine. Benzoyl chloride, however, readily gave the benzoyl derivative. Chloroacetyl chloride on heating with phosphanilic acid gave a product which was decomposed by water and hence could not be identified.

Phosphanilic acid was diazotised and coupled with resorcinol, pyrrole and *m*-phenylenediamine when the corresponding azo dyes were obtained.

Preparation of carbamidophosphanilic acid could not be carried out by heating with potassium cyanate or cyanogen bromide. The ammonium salt of the compound, however, was obtained by heating urea with phosphanilic acid.

Attempts were made to prepare phosphanilamide, the analogue of sulphanilamide. *p*-Bromophenylphosphinyl amide (prepared from *p*-bromophenylphosphonyl oxychloride, $\text{BrC}_6\text{H}_4\text{POCl}_2$, and ammonia) gave the amide in low yield by heating with aqueous ammonia in presence of cuprous oxide. Similar attempts to prepare the analogue of sulphathiazole failed.

The diethylamine and ethanolamine salts of phosphanilic acid were prepared by treating the acid with the appropriate amine, followed by crystallisation from water. The salts contain two equivalents of the base for one molecule of the acid, as shown by the analysis.

Benzaldehyde did not react with phosphanilic acid on heating without a solvent or in alcoholic solution, but gave the anil in a low yield when heated in the presence

of anhydrous zinc chloride. However, the anil was unstable and could not be obtained pure.

The antibacterial properties of these compounds have been already reported (Bhide and Kanitkar, *Curr. Sci.*, 1947, **16**, 223). None of these derivatives has been found to be superior to phosphanilic acid in antibacterial properties.

Phosphanilic acid has been found to inhibit completely the growth of *M. tuberculosis in vitro* in a concentration of 1:5000. Preliminary pharmacological tests show that phosphanilic acid is comparatively non-toxic to laboratory animals and is little absorbed in the blood (unpublished work).

EXPERIMENTAL

Phosphanilic Acid.—*p*-Bromophenylphosphinic acid (6 g.), freshly prepared cuprous oxide (4.5 g.) and ammonia (d 0.88, 100 c.c.) were heated on a water-bath till all the cuprous oxide dissolved (10 hours). On removal of the copper as copper sulphide by passing H_2S , the solution was made acidic to Congo red, when a granular precipitate of phosphanilic acid was obtained. On purifying according to Bauer it melted at 245° .

The acetyl and benzoyl derivatives of phosphanilic acid were prepared by treating a solution of the acid in sodium bicarbonate with acetic anhydride and benzoyl chloride respectively. The acetyl derivative had m. p. 229° (cf. Bauer, *loc. cit.*).

Benzoyl derivative was purified by dissolving it in sodium bicarbonate and precipitating with acid, m. p. 287° . It is insoluble in the usual organic solvents and is sparingly soluble in acetone. (Found : N, 5.23. $C_{13}H_{12}O_4NP$ requires N, 5.05 per cent).

Succinylphosphanilic Acid.—Phosphanilic acid (1 g.), dissolved in the minimum quantity of sodium bicarbonate, was shaken with succinic anhydride (2 g.) till the solution did not give the test for a primary amine with *p*-dimethylaminobenzaldehyde. The solution on acidification to Congo red with hydrochloric acid was evaporated to dryness. The residue was soxhleted with ether to remove free succinic acid. The residue, easily soluble in water and insoluble in organic solvents, on recrystallisation from water melted at 276° . (Found : N, 5.36; equiv., 93. $C_{10}H_{12}O_6NP$ requires N, 5.13 per cent. Equiv., 91).

Butyrylphosphanilic acid is insoluble in water and in the common organic solvents, m. p. 284° . (Found : N, 5.81. $C_{10}H_{14}O_4NP$ requires N, 5.76 per cent).

Caproylphosphanilic acid crystallises from dioxan, m. p. 204° . (Found : N, 5.36. $C_{12}H_{18}O_4NP$ requires N, 5.16 per cent).

Azo dyes from Phosphanilic Acid.—To phosphanilic acid (1 g.) in 5*N*-HCl (2 c.c.) sodium nitrite (0.4 g.) was added, followed by resorcinol (0.63 g.), dissolved in sodium hydroxide, keeping the temperature at 0° . A red dye was obtained, melting at 211° . (Found : N, 9.3. $C_{12}H_{11}O_5N_2P$ requires N, 9.52 per cent).

An azo dye, violet in colour and without any definite melting point, was obtained from pyrrole and phosphanilic acid in an analogous manner. (Found : N, 16.63. $C_{10}H_{10}O_3N_3P$ requires N, 16.73 per cent).

m-Phenylenediamine gave a red dye having no definite melting point. (Found: N, 18.87. $C_{12}H_{13}O_3N_4P$ requires N, 19.18 per cent).

Ammonium salt of Carbamidophosphanilic Acid.—Phosphanilic acid (1 g.) and urea (0.6 g) were heated at 120° for 6 hours. The resulting product was extracted with alcohol to remove urea. The residue was dissolved in water with the addition of dilute ammonia and evaporated to dryness. The resulting solid did not give a test for a free primary amino group. It does not melt up to 300° . The nitrogen content and the absence of a primary amino group indicate that the compound is, in all probability, the ammonium salt of carbamidophosphanilic acid. (Found: N, 17.92. $C_7H_{12}O_4N_3P$ requires N, 18.03 per cent).

Amide of Phosphanilic Acid—*p*-Bromophenylphosphonyl chloride was treated with ice-cold concentrated ammonia. A white precipitate of the diamide of *p*-bromophenylphosphinic acid slowly separated. The precipitate was filtered and washed with water. It crystallised from alcohol in plates and melted to a turbid liquid at 202° which became clear at 256° . (Found: N, 12.11. $C_6H_8OBrN_2P$ requires N, 11.91 per cent).

The above amide (8 g) and freshly prepared cuprous oxide (8 g.) were heated on the water-bath with ammonia (d 0.88, 150 c.c.) till all the cuprous oxide dissolved. It was then acidified, copper removed as sulphide, and the solution treated with sodium bicarbonate till the solution was slightly acidic to Congo red, when a white precipitate settled down. It was purified by dissolving it in acid, treating with animal charcoal and precipitating with bicarbonate solution. It was then obtained in a snow white form, m. p. 224° . A little over two equivalents of ammonia were evolved on heating it with sodium hydroxide. It did not analyse satisfactorily for nitrogen by Dumas method. It was, in all probability, the diamide, as it was insoluble in bicarbonate solution and gave all the tests for a free primary amino group. [Found: N (as ammonia), 17.5. $C_6H_{10}ON_4P$ requires N 16.38 per cent].

Reaction of 2-Aminothiazole with p-Bromophenylphosphonyl Chloride.—*p*-Bromophenylphosphonyl chloride (27 g.) and 2-aminothiazole (22 g.) were mixed in dry benzene with cooling. After allowing it to stand overnight it was refluxed on a water-bath for 2 hours. On removal of benzene, a black residue was obtained which was treated with sodium carbonate. It was boiled and filtered hot. The filtrate on cooling gave a brown solid. On treating it with animal charcoal it crystallised from water, m. p. 187° .

The free acid was obtained from the above sodium salt by dissolving in the minimum quantity of concentrated hydrochloric acid and on addition of absolute alcohol followed by ether. It melts at 225° . It is soluble in water and alcohol but insoluble in ether. (Found: N, 8.93. $C_9H_8O_2BrN_2PS$ requires N, 8.78 per cent).

The acid gave a picrate, m. p. 232° . (Found: N, 12.58. $C_{13}H_{11}O_5BrN_3PS$ requires N, 12.8 per cent).

Diethylamine Salt of Phosphanilic Acid.—Phosphanilic acid (1 g.) was suspended in water and diethylamine (1 c.c.) was added to it. It was warmed on the water-bath for half an hour. The diethylamine salt slowly crystallised from water in needles melting at 212° . (Found : N, 12.96. $C_{14}H_{20}O_3N_2P$ requires N, 13.16 per cent).

Ethanolamine salt was prepared in a similar manner and crystallised in plates from water m. p. 178° . (Found : N, 13.97. $C_{10}H_{22}O_4N_2P$ requires N, 14.24 per cent).

MAHARAJA PRATAPSIKH CHEMICAL LABORATORY,
SIR PARASHURAMBHAU COLLEGE, POONA.

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KINETICS OF THE DEVELOPMENT OF THE JOSHI EFFECT IN CHLORINE UNDER SILENT ELECTRIC DISCHARGE

By M. V. RAMANAMURTHI

The progressive development of the Joshi effect, Δi , during 'ageing' under discharge in freshly prepared chlorine-filled ozonisers, follows the equation for the 'first order' reactions. It is suggested that chemisorption, involving electron transference, is responsible for the formation of the excited boundary layer postulated in Joshi's theory of the phenomenon. The continued increase in the Joshi effect to a stationary maximum is attributed to a diminution with time of the 'work function' characteristic of the excited layer formed under discharge, and which is the chief seat of the Joshi effect

The significance of the time variation of the electrical quantities for an analysis of the corresponding discharge reaction has been emphasized by Joshi (*Curr. Sci.*, 1939, 8, 548; Deshmukh and Kane, *Proc. Ind. Acad. Sci.*, 1947, 28A, 247; Deo, *ibid.*, 1945, 21A, 76). The observation (Joshi, *Proc. Indian Sci. Cong.*, 1943, Part II, Sec. III, p. 51) therefore, that the Joshi effect viz., an instantaneous and reversible diminution, Δi , of the discharge current i on irradiation of the discharge tube, is influenced markedly by ageing under a constant applied field, appeared to be of interest. It is found, e.g., that a Joshi effect corresponding to 14 to 50% current diminution by exposure to but ordinary light, develops progressively under discharge (*vide infra*). Such continued increase of Δi under ageing at sensibly constant exciting conditions (*vide infra*) corresponds to the progress of a chemical change. Following Joshi's finding (*Curr. Sci.*, 1945, 14, 175) that the course of a discharge reaction may be envisaged from the standpoint of the law of mass action, kinetic studies for the growth of the Joshi effect, Δi , are now made for the first time in this field.

EXPERIMENTAL

The general arrangement of the apparatus for the production of the electrical discharge in chlorine is shown in Fig. 1. A number of Siemens' type (glass) ozonisers were prepared by Prof. Joshi and filled with chlorine at gas pressures adjusted by him for the maximum effect Δi under short durations (not exceeding 30 sec. at a time) of exposure to the discharge. This restriction of time served to minimise the effect due to ageing now investigated. The results for the Joshi effect Δi refer to three from the above batch of ozonisers filled with the gas at 220 mm. pressure. They were excited under various applied fields and the discharge current i was observed at regular intervals by means of a reflection galvanometer actuated by a diode 83V (RCA), when the ozoniser was in the dark, (i_0) and when irradiated externally from an incandescent

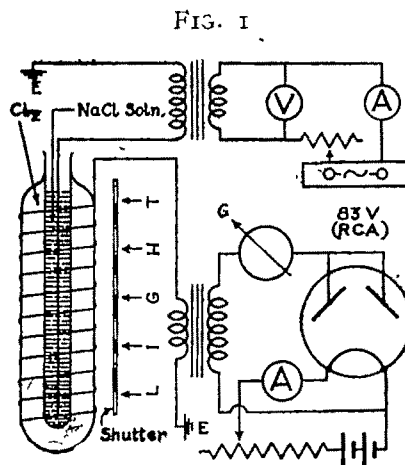


TABLE I

T (mins.)	Ozoniser A				Ozoniser B				Ozoniser C							
	i_a	$\Delta i.$	k_a ($\times 10^3$).	$\% \Delta i.$	k'_a ($\times 10^3$).	i_b	u_b	$\Delta i.$	k_b ($\times 10^3$).	$\% \Delta i.$	k'_b ($\times 10^3$).	i_c	$\Delta i.$	k_c ($\times 10^3$).	$\% \Delta i.$	k'_c ($\times 10^3$).
0	93	53	40 (40)	43.0 (43.0)		666	493	173 (174)		26.4 (26.4)		407	350	57 (60)	14.0 (14.0)	
5	91	50	41 (40.7)	43.8 (44.0)	3.09	—	—	182 (182)	2.58	(28.5)	2.10	438	368	70 (70)	15.9 (15.6)	1.15
10	—	—	41.2 (41.2)	45.4 (45.4)	4.19	622	435	187 (190)	2.78	30.6 (30.0)	2.21	465	381	84 (80)	17.5 (17.2)	1.31
15	—	—	41.9 (41.9)	45.9 (45.9)	3.76	—	—	195 (195)	2.54	(32.3)	2.19	—	—	90 (90)	18.4 (18.5)	1.15
20	89	47	42 (42.5)	46.5 (46.7)	3.76	575	370	205 (200)	2.50	36.0 (35.0)	2.18	—	—	96 (96)	17.0 (19.9)	1.16
30	92	48	44 (43.5)	48.0 (48.0)	3.77	548	441	207 (207)	2.50	38.1 (38.1)	2.20	495	385	110 (110)	22.5 (22.4)	1.16
45	92	47	45	49.0		568	341	227		40.5		500	368	132 (130)	26.4 (26.0)	1.15

TABLE I. (contd.)

Ozoniser A										Ozoniser B				Ozoniser C				
T (mins.)	t_D	t_L	Δt	k_A ($\times 10^3$).	% Δt	k'_A ($\times 10^3$).	t_D	t_L	Δt	k_B ($\times 10^3$).	% Δt	k'_B ($\times 10^3$).	t_D	t_L	Δt	k_C ($\times 10^3$).	% Δt	k'_C ($\times 10^3$).
60	82	42	40	49.5			581	337	244		41.9		525	365	140 (140)	1.67	28.0 (28.9)	1.19
90	94	49	46	48.5			576	332	244		42.4		411	291	150		34.5	
120	91	45	46	49.5			506	276	230		45.5		430	264	166		38.5	
150	94	47	47	50.0			506	268	238		47.0		432	260	172		39.8	
180	96	49	47	49.0			504	270	234		47.5		429	248	181		42.0	
210	96	48	48	50.0			505	267	238		47.5		429	247	182		42.5	
240	96	48	48	50.0			509	269	240		47.5		437	250	187		42.8	
270	96	48	48	50.0			509	268	241		47.5		431	246	185		42.5	
300	96	48	48	50.0			509	268	241		47.5		431	246	185		42.5	
				(50.0)					(24.5)		(47.5)				(185)		(42.5)	

The quantities within the brackets were read off from the Δt -time and % Δt -time curves in Fig. 2, and used in calculating k and k' for early stages of 'ageing' under the discharge.

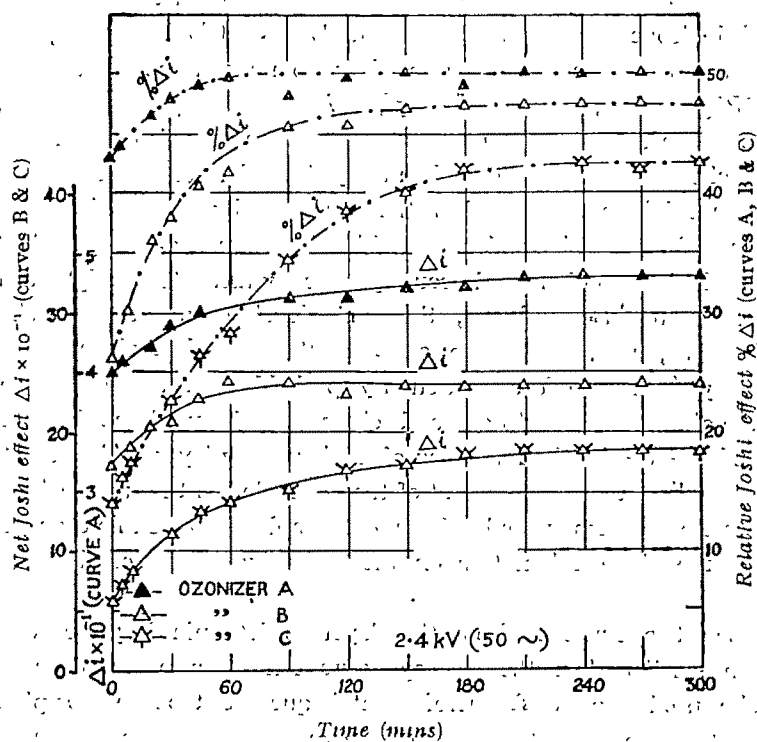
100 watt, 220 volt (glass) bulb, (i_L). From these data the net Joshi effect, $\Delta i = (i_b - i_L)$, and its relative value $\% \Delta i = \frac{100 \cdot \Delta i}{i_b}$ were calculated. The results obtained in all cases were essentially similar. They have been sufficiently represented by one typical group of data given in Table I and in part in Fig. 2, corresponding to an exciting potential 2.4 kV of 50 cycles frequency at the room temperature (27°).

DISCUSSION

The theory of the above effect Δi , as advanced by Joshi (*Proc. Indian Sci. Cong*, Part III, 1946, *Phys. Sécl., Abst. No. 26*; *Curr. Sci.*, 1947, **16**, 19) contemplates three stages, viz., (i) a boundary layer is formed on the container walls, derived in part, from adsorption of ions and excited molecules under the applied fields, when intense enough to break down the gas dielectrically, at the threshold potential V_m ; (ii) photo-electric emission occurs from this boundary layer under external irradiation; and (iii) these photo-electrons are captured by the *excited* neutral molecules to form slow moving negative ions which are responsible for the current decrease, Δi , as a space charge effect (Joshi, *loc. cit.*)

Work in these laboratories has shown that the boundary layer contemplated in (i) is fundamental not only to the Joshi effect but a number of other phenomena e.g., 'ageing' and the newly observed periodic effect in N_2O-H_2 and other reactions under electrical discharges. Since the stages (ii) and (iii) are instantaneous and fully reversible, it would follow that *ceteris paribus*, a time-variation in the magnitude of Δi under 'ageing' is determined practically entirely by the extent to which stage (i) occurs, and hence the curves, Δi , ($\% \Delta i$)—time, represent the course of the reaction occurring in stage (i). Significantly, the Joshi effect (Δi) and its relative value ($\% \Delta i$) in all the cases were found to increase *progressively*; they, however, became stationary after exposure of about five hours to discharge depending upon the operative conditions (*cf.* curves in Fig. 2). The difference of the final stationary value for Δi (or $\% \Delta i$) and the value at the commencement viz., Δi_0 (or $\% \Delta i_0$) measures the total net production of the change and corresponds to the initial concentration term 'a' in the familiar equations for the (chemical) reaction-velocities. Similarly, the difference of Δi_t (or $\% \Delta i_t$) at any time t and Δi_0 (or Δi_0) is a measure of 'x', the amount changed. The results given in Table I show that the values of Δi (or $\% \Delta i$), reckoned since the commencement of 'ageing' under discharge for each of the three ozonisers A, B and C, yield a sensibly constant value for the velocity coefficient 'k', when the equation for first order reactions is used. It may be mentioned that the values for Δi (and $\% \Delta i$) used in the calculation of the velocity coefficient, k , were read off from the smooth curves in Fig. 2 and are shown in parenthesis below the actually observed corresponding quantities in Table I. The above constancy in the unimolecular coefficient (k) also applied to the results (not shown) obtained with the ozonisers A, B and C at potentials other than the one to which Table I and Fig. 2 refer. This remark again applied to corresponding results (not shown) obtained with the other ozonizers, i.e., besides A, B and C. The data in Table I show that during the periods over which the velocity coefficients, k

FIG. 2



and k' , have been calculated, the current in dark, i_0 , and the same under light, i_L , do not show an identical time-variation, thus e.g., with the ozonisers A and B both the above quantities show a progressive decrease with time; the ozoniser C, however, shows the opposite. The significant result that the time-variation in respect of both Δi and $\% \Delta i$ yields series of constant velocity coefficients suggests that the Joshi effect is more a characteristic of the boundary layer than of the conductivities in dark and under light.

In view of the above observation that Δi under ageing progresses according to the unimolecular law for chemical reactions, it is suggested that the type of adsorption involved in the formation of the boundary layer postulated by Joshi for stage (i) may be predominantly 'chemical' in nature. McBain ("The Sorption of Gases by Solids," Routledge, 1932) has pointed out that sorption of gases occurring on solids under normally "unfavourable" conditions e.g., high temperatures, is due to energised molecules or atoms being attached to the solid surface with electron transference, which is observed markedly in the case of elements like chlorine, bromine and oxygen. It is found by James Taylor (*Nature*, 1928, 121, 708; *ibid.*, 1928, 122, 347) that a passage of electric discharge through a gas favours condensation e.g., a large and progressive decrease, to a slight trace finally, of the hydrogen content (indicated spectrographically) in hydrogen-neon tubes was observed when the tubes were excited. His experiments on helium again has shown that the disappearance of the gas under discharge is not due to an accelerated diffusion through the pores of the glass

wall. He attributed this to sorption of the gas on the container walls. This he preferred to the concept of a purely physical adsorption. From the studies of the regular contraction of hydrogen under discharge, De Laplace (*Compt. rend.*, 1928, **187**, 225) showed that it was not due to the formation of triatomic hydrogen. The experiments of Hill (*Proc. Phys. Soc.*, 1912, **25**, 35), Willows and George (*ibid*, 1916, **28**, 124) on sorption of gases in vacuum tubes under discharge also confirmed that it was a result of a chemical action. This boundary layer formed under discharge therefore is to be discriminated from physical adsorption attributed by Langmuir to the operation of van der Waals forces, which is determined by the pressure of the gas, the temperature and the mass of the adsorbent and occurs practically *instantaneously* and cannot therefore be fundamental to 'ageing' *i.e.*, the time development of the Joshi effect, Δi . Hence the other type, *viz.*, chemisorption associated with the molecules possessing high activation energy (and therefore particularly probable under a discharge reaction), formed with the aid of valency forces and characterised by a large heat of adsorption, should be fundamental for the formation of the boundary layer. This excited gas layer on the electrode walls therefore is a result of the molecules on the surface being activated due to the ionic bombardment under discharge at a fixed applied field and consequently undergoing a more stable condensation on the walls by means of distorted 'electron transference.'

The photoelectric emission from this layer is determined by the 'work function' which is much smaller than the corresponding ionisation potential in the gaseous condition. The production of Δi therefore, at frequencies too small for photo ionisation follows (Joshi, *Curr. Sci.*, 1947, **16**, 19). With continuous activation due to ionic bombardment under the discharge (*i.e.* during 'ageing' under the discharge) the work function should diminish and the relative Joshi effect increase correspondingly to a stationary maximum as observed.

The author takes this opportunity to express his grateful thanks to Prof. S. S. Joshi, D.Sc., F.R.I.C., F.N.I., for suggesting the problem and for the keen and valuable guidance during the work.

DEPARTMENT OF CHEMISTRY,
BENARES HINDU UNIVERSITY.

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GROUP PARACHORS BY GIBLING'S METHOD. PART II.

BY W. V. BHAGWAT AND G. V. BAKORE.

Group parachors for the groups $\text{C}-\text{CH}_2-\text{OH}$ (69.7); $\text{C}-\text{C}\equiv\text{N}$ (66.7); $\text{C}\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C}=\text{O}$ (72.7); $\text{C}\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C}=\text{O}\cdot\text{NH}_2$ (91.07); $\text{C}\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C}=\text{CH}_2\cdot\text{NO}_2$ (115.75); $\text{C}-\text{CH}_2-\text{O}\cdot\text{NO}$ (115.32) and $\text{C}\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C}-\text{N}\equiv\text{C}$ (53.1) have been determined. It is observed that even group parachors are not constant in the same homologous series. Introduction of a ring or a branch chain or increase in length of the carbon chain lowers the group parachor. For isomerides the effect of length of the straight chain is more marked than of the branch chain or a ring.

In previous papers (*J. Indian Chem. Soc.*, 1945, **22**, 115, 222; 1948, **25**, 175) structural parachors for certain groups by Gibling's method have been evaluated. The work is extended in this paper to other groups.

Group Parachor for $\text{C}-\text{CH}_2-\text{OH}$

TABLE I

Compound.	$P_{\text{obs.}}$	R. C.	Groups subtracted	$P_{\text{for (C)-CH}_2-\text{OH}}$
Ethyl alcohol	127.5	0.1	$\text{CH}_3-(\text{C})$	71.7
$\text{CH}_3-\text{CH}_2\cdot\text{OH}$	127.3			
	126.8			
	126.6			
Mean	127.0			
Allyl alcohol	152.7	0.2	$\text{CH}_2=(\text{C}), (\text{C})=\text{CH}(\text{C})$	69.0
$\text{CH}_2=\text{CH}\cdot\text{CH}_2\cdot\text{OH}$	153.8			
Mean	153.2			
<i>n</i> -Propyl alcohol	165.4	0.2	$\text{CH}_3-(\text{C})$ and	70.2
$\text{CH}_3-\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$	165.8		$(\text{C})-\text{CH}_2-(\text{C})$	
	164.7			
Mean	165.4			
<i>n</i> -Butyl alcohol	202.9	0.4	$\text{CH}_3-(\text{C})$ and	68.0
$\text{CH}_3-(\text{CH}_2)_2\cdot\text{CH}_2\cdot\text{OH}$	203.4		$2(\text{C})-\text{CH}_2-(\text{C})$	
Mean	203.2			
<i>iso</i> -Butyl alcohol	202.1	0.4	$2\text{CH}_3-(\text{C})$ and	69.1
$\text{CH}_3\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{CH}\cdot\text{CH}_2\cdot\text{OH}$			$(\text{C})\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{CH}(\text{C})$	
$\text{CH}_3\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{CH}\cdot\text{CH}_2\cdot\text{OH}$			$(\text{C})\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{CH}(\text{C})$	
<i>n</i> -Amyl alcohol	243.3	0.6	$\text{CH}_3-(\text{C})$ and	68.1
$\text{CH}_3-(\text{CH}_2)_3\cdot\text{CH}_2\cdot\text{OH}$			$3(\text{C})-\text{CH}_2-(\text{C})$	
<i>iso</i> -Amyl alcohol	241.4	0.6	$2\text{CH}_3-(\text{C})$ and	68.4
$\text{CH}_3\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{CH}-\text{CH}_2-\text{CH}_2\cdot\text{OH}$			$(\text{C})\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{CH}(\text{C})$	
$\text{CH}_3\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{CH}-\text{CH}_2-\text{CH}_2\cdot\text{OH}$			$(\text{C})\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{CH}(\text{C})$	

TABLE I (contd.)

Compound.	$P_{\text{obs.}}$	E. C	Groups subtracted	$P_{\text{for C-CH}_2\text{-OH.}}$
<i>ter.</i> Amyl alcohol $\begin{array}{c} \text{CH}_3 \diagup \text{C} \diagdown \text{CH}_3 \\ \text{CH}_3 \diagdown \text{C} \diagup \text{CH}_2\text{OH} \end{array}$	241.1	0.6	3CH_3 (C) and $\begin{array}{c} \text{(C)} \diagup \text{C} \diagdown \text{(C)} \\ \text{(C)} \diagdown \text{C} \diagup \text{(C)} \end{array}$	72.5
Benzyl alcohol $\text{C}_6\text{H}_5\text{-CH}_2\text{OH}$	259.6	0.7	$5(\text{C})-\text{CH}=(\text{C})$ and $\begin{array}{c} \text{(C)} \\ \\ \text{C}-(\text{C}) \\ \\ \text{(C)} \end{array}$	70.7
<i>n</i> -Hexyl alcohol $\text{CH}_3-(\text{CH}_2)_4\text{-CH}_2\text{OH}$	276.2	0.7	$\text{CH}_3-(\text{C})$ and $4(\text{C})-\text{CH}_2-(\text{C})$	61.1
<i>n</i> -Heptyl alcohol $\text{CH}_3-(\text{CH}_2)_5\text{-CH}_2\text{OH}$	313.1	0.9	$\text{CH}_3-(\text{C})$ and $5(\text{C})-\text{CH}_2-(\text{C})$	58.3
<i>n</i> -Octyl alcohol $\text{CH}_3-(\text{CH}_2)_6\text{-CH}_2\text{OH}$	354.4	1.2	$\text{CH}_3-(\text{C})$ and $6(\text{C})-\text{CH}_2-(\text{C})$	59.2

Mean 66.7

In taking mean for the parachor of $(\text{C})-\text{CH}_2\text{OH}$ group, the last three values, which show very great deviation, are omitted. The following table illustrates that the structural parachors for groups reproduce experimental results better than Sugden's values. The values substituted in the last three compounds obviously show a great deviation from the observed values, but even then they approach experimental values more than Sugden's values.

TABLE II

Compound	P (Structural)	$P_{\text{obs.}}$	P (Sugden)
Ethyl alcohol	125	127.5, 127.3 126.8, 126.6	132.2
Allyl alcohol	153.9	152.7, 153.8 165.4, 165.8	160.2
<i>n</i> Propyl alcohol	164.9	165.4, 165.8 and 164.7	171.2
<i>n</i> -Butyl alcohol	204.9	202.9, 203.4	210.2
<i>iso</i> Butyl alcohol	202.7	202.1	210.2
<i>n</i> -Amyl alcohol	244.9	243.3	249.2
<i>iso</i> Amyl alcohol	242.6	241.4	249.2
<i>ter.</i> Amyl alcohol	238.3	241.1	249.2
Benzyl alcohol	258.6	259.6	266.1
<i>n</i> -Hexyl alcohol	267.6	276.2	288.2
<i>n</i> -Heptyl alcohol	302	313.4	327.2
<i>n</i> -Octyl alcohol	343.9	354.4	366.2

Group Parachor for $C-CN$ or $C-C\equiv N$

TABLE III

Compound.	P _{obs.}	R. C.	Groups subtracted.	P for (C)-CN.
Propionitrile CH_3-CH_2-CN	160.5	0.2	$CH_3-(C)$, $(C)-CH_2-(C)$	65.3
n-Butyronitrile $CH_3-(CH_2)_2-CN$	210.2	0.4	$CH_3-(C)$ and $2(C)-CH_2-(C)$	66.0
isoValeronitrile $\begin{array}{c} CH_3 \\ \diagup \\ CH-CH_2-CN \\ \diagdown \\ CH_3 \end{array}$	237.4	0.5	$2CH_3-(C)$, $(C) \begin{array}{c} \diagup \\ CH-(C) \\ \diagdown \end{array}$ and $(C)-CH_2-(C)$	64.5
Benzonitrile C_6H_5-CN	255.5	0.7	$5(C)-CH=(C)$ and $(C) \begin{array}{c} \diagup \\ C=(C) \\ \diagdown \end{array}$ $(C) \begin{array}{c} \diagup \\ C=(C) \\ \diagdown \end{array}$	66.6
Phenylacetoneitrile $C_6H_5-CH_2-CN$	293.6 293.4	0.9	$5(C)-CH=(C)$, $(C)-CH_2-(C)$ and $(C) \begin{array}{c} \diagup \\ C=(C) \\ \diagdown \end{array}$ $(C) \begin{array}{c} \diagup \\ C=(C) \\ \diagdown \end{array}$	64.6
o-Toluenitrile $CH_3-C_6H_4-CN$	292.5 292.9	0.9	$4(C)-CH(C) \begin{array}{c} (C) \\ \diagup \\ C=(C) \\ \diagdown \end{array}$ and $(C)-CH_3$	65.3
Mean	290.6 292.6			
n-Valeronitrile $CH_3-(CH_2)_3-CN$	236.6 237.4 Mean 237.0	0.5	$CH_3-(C)$ and $3(C)-CH_2-(C)$	61.9
n-Capronitrile $CH_3-(CH_2)_4-CN$	276.6	0.7	$CH_3-(C)$ and $4(C)-CH_2-(C)$	61.5
isoButylacetoneitrile $(CH_3)_2CH-CH_2-CH_2-CN$	275.0	0.7	$2CH_3-(C)$, $(C) \begin{array}{c} \diagup \\ CH-(C) \\ \diagdown \end{array}$ and $2(C)-CH_2-(C)$	62.5
n-Heptonitrile $CH_3-(CH_2)_5-CN$	316.1	0.9	$CH_3-(C)$ and $5(C)-CH_2-(C)$	61.0
n-Nononitrile $CH_3-(CH_2)_7-CN$	395.2	1.5	$CH_3-(C)$ and $7(C)-CH_2-(C)$	59.9
n-Octylic nitrile $CH_3-(CH_2)_6-CN$	356.0	1.2	$CH_3-(C)$ and $6(C)-CH_2-(C)$	60.8
m-Toluenitrile $CH_3-C_6H_4-CN$	295.6	0.8	$4(C)-CH=(C)$, $(C)-CH_3$ and $(C) \begin{array}{c} \diagup \\ C=(C) \\ \diagdown \end{array}$ $(C) \begin{array}{c} \diagup \\ C=(C) \\ \diagdown \end{array}$	69.0
p-Toluenitrile $CH_3-C_6H_4-CN$	295.2 295.9 294.4 Mean 295.2	0.8	"	68.6
Mean				Mean 66.7

Lower members of the series alone are considered on taking mean, as higher members give very low values.

In the following table the values obtained by Sugden's method and by our method are compared with the observed values. The values obtained by introducing group parachors show better agreement with the experimental results in the case of lower members of the homologous series which were considered in taking mean.

TABLE IV

Compound.	P (Structural).	P _{obs.}	P (Sugden).
Propionitrile	161.9	160.5	159.0
<i>n</i> -Butyronitrile	201.9	201.2	198.0
<i>iso</i> -Valeronitrile	239.6	237.4	237.0
Benzonitrile	255.6	255.5	253.9
Phenylacetoneitrile	294.7	293.6, 293.4	292.9
<i>o</i> -Tolunitrile	293.4	292.5, 292.9, 290.6	292.9
<i>n</i> -Valeronitrile	241.8	236.6, 237.4	237.0
<i>n</i> -Capronitrile	281.8	276.6	276
<i>iso</i> -Butylacetoneitrile	279.2	275.5	276
<i>n</i> -Heptonitrile	321.8	316.9	315
<i>n</i> -Nononitrile	402	395.2	393
<i>n</i> -Octylic nitrile	361.9	356.0	354
<i>m</i> -Tolunitrile	293.7	295.6	292.9
<i>p</i> -Tolunitrile	293.3	295.2, 295.9 294.4	292.9

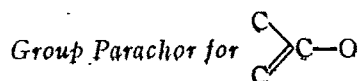
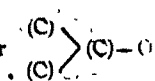


TABLE V

Compound.	P _{obs.}	R. C.	Groups subtracted.	P for 
Anisole <chem>C6H5-O-CH3</chem>	265.6	0.7	5 (C)—CH= (C) and (C)—O— (C)	71.9
<i>o</i> -Nitroanisole	322.1	0.9	4 (C)—CH= (C), (C)—C NO ₂ = (C) and (C)—O— (C)	72.9
<i>p</i> -Nitroanisole	322.6	0.9	"	73.4 Mean 72.7

The parachors obtained by structural and Sugden's method are compared with the experimental values.

TABLE VI

Compound.	P (Structural).	P _{obs.}	P (Sugden).
Anisole	266.4	265.6	266.1
<i>o</i> -Nitroanisole	321.9	322.1	324.7
<i>p</i> -Nitroanisole	321.9	322.6	324.7

Group Parachor for $C-\text{CONH}_2$

TABLE VII

Compound.	$P_{\text{obs.}}$	E. C.	Group subtracted.	P for $(C)-\text{CH}_2-\text{OH}$.
Acetamide CH_3CONH_2	148.0	0.2	$\text{CH}_3-(C)$	92.6
Propionamide $\text{CH}_3-\text{CH}_2\text{CONH}_2$	181.2	0.3	$\text{CH}_3-(C), (C)-\text{CH}_2-(C)$	85.9
Benzamide $\text{C}_6\text{H}_5\text{CONH}_2$	279.9	0.7	$5(C)-\text{CH}=(C), (C) \begin{array}{l} \diagup \\ \diagdown \end{array} \text{C}=(C)$	91.0
Salicylamide $\text{C}_6\text{H}_4(\text{OH})\text{CONH}_2$	295.3	0.8	$4(C)-\text{CH}=(C), (C) \begin{array}{l} \diagup \\ \diagdown \end{array} \text{C}=(C)$ $(C)=C \begin{array}{l} \diagup (C) \\ \diagdown \text{OH} \end{array}$	94.63
Phenylacetamide $\text{C}_6\text{H}_5-\text{CH}_2\text{CONH}_2$	320.2	1.0	$5(C)-\text{CH}=(C), (C)-\text{CH}_2-(C)$ and $(C) \begin{array}{l} \diagup \\ \diagdown \end{array} \text{C}=(C)$	91.2
				Mean 91.07

The structural parachor values and those obtained from Sugden's method are compared with the observed values in the following table.

TABLE VIII

Compound.	P (Structural).	$P_{\text{obs.}}$	P (Sugden)
Acetamide	146.07	148.0	150.8
Propionamide	186.37	181.2	189.8
Benzamide	279.97	279.9	284.7
Salicylamide	291.74	295.3	304.7
Phenylacetamide	320.07	320.2	323.7

Group Parachor for $C-\text{CH}_2-\text{NO}_2$ or $C-\text{CH}_2-\text{N} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$

TABLE IX

Compound.	$P_{\text{obs.}}$	E. C.	Groups subtracted.	P for $(C)-\text{CH}_2-\text{NO}_2$.
Nitroethane $\text{CH}_3-\text{CH}_2\text{NO}_2$	171.2	0.25	$\text{CH}_3-(C)$	115.75

Parachor calculated by structural method is 171.2 and those calculated by Sugden's method is 170.8. The work needs further confirmation.

Group Parachor for $C-\text{CH}_2-\text{O}-\text{NO}$
(Nitrite group)

TABLE X

Compound.	$P_{\text{obs.}}$	E. C.	Groups subtracted.	P $(C)-\text{CH}_2-\text{O}-\text{NO}$.
<i>n</i> -Butyl nitrite $\text{CH}_3-(\text{CH}_2)_3-\text{CH}_2\text{O}\cdot\text{NO}$	251.8	0.6	$\text{CH}_3-(C), 2(C)-\text{CH}_2-(C)$	116.4
<i>iso</i> -Amyl nitrite $(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{CH}_2\text{O}\cdot\text{NO}$	287.4	0.75	$2\text{CH}_3-(C), (C) \begin{array}{l} \diagup \\ \diagdown \end{array} \text{CH}-(C)$ and $(C)-\text{CH}_2-(C)$	114.25
				Mean 115.34

The structural parachor values and those obtained from Sugden's method are compared with the observed values in the following table.

TABLE XI

Compound.	P (Structural).	P _{obs.}	P (Sugden).
<i>n</i> -Butyl nitrite	250.72	251.8	248.8
<i>iso</i> Amyl nitrite	288.47	287.4	287.8

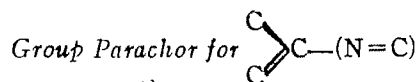


TABLE XII

Compound.	P _{obs.}	H. C.	Groups subtracted.	P $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{C}-\text{N}=\text{C}$
Phenyl isocyanide $\text{C}_6\text{H}_5.\text{NC}$	255.2	0.6	5(C) = CH—(C)	83.1
<i>o</i> -Tolyl isocyanide $\text{CH}_3.\text{C}_6\text{H}_4.\text{NC}$	292.9	0.8	4(C) = CH—(C), (C) $\begin{array}{c} \diagup \quad \diagdown \\ \text{C} \end{array} \text{C} = (\text{C})$ and $\text{CH}_3-(\text{C})$	83.0
<i>p</i> -Tolyl isocyanide	295.5	0.8	$\text{CH}_3-(\text{C})$, 4(C) — CH = (C)	85.4
Mean	295.0 295.3		(C) $\begin{array}{c} \diagup \quad \diagdown \\ \text{C} \end{array} \text{C} = (\text{C})$	
<i>o</i> -Anisyl isocyanide $\text{O}.\text{CH}_3.\text{C}_6\text{H}_4.\text{NC}$	314.1	0.9	(C)—O—(C), 4(C) — CH = (C), (C) = C—O	81.8
<i>p</i> -Anisyl isocyanide	314.5 315.0	0.9	(C)—O—(C), 4(C) — CH = (C), (C) $\begin{array}{c} \diagup \quad \diagdown \\ \text{C} \end{array} \text{C} = \text{O}$	82.2
			Mean	83.1

The values obtained by structural and Sugden's methods are compared with the observed values in the following table.

TABLE XIII

Compound.	P (Structural)	P _{obs.}	P (Sugden).
Phenyl isocyanide	255.2	255.2	230.5
<i>o</i> -Tolyl isocyanide	293.0	292.9	269.5
<i>p</i> -Tolyl isocyanide	293.0	295.5, 295.0	269.5
<i>o</i> -Anisyl isocyanide	315.4	314.1	289.5
<i>p</i> -Anisyl isocyanide	315.4	314.5, 315.0	289.5

Structural values are in close agreement with the observed values. The evaluation of group parachors again reveals that the values are not constant even for the same homologous series, but fall as we ascend the series. The increase in the length of the carbon chain lowers the parachor value of the group. For isomeric compounds the lowering caused by the branch chain is less than the straight chain. The same is true if a ring is introduced instead of a branch chain.

STUDIES ON THE CIRCULAR DICHROISM AND ROTATORY DISPERSION. PART III. MEASUREMENT OF ABSORPTION, CIRCULAR DICHROISM AND ROTATORY DISPERSION OF POTASSIUM VANADYL *d*-TARTRATE

By B. C. KAR

Potassium vanadyl *d*-tartrate has been prepared and the measurement of absorption, circular dichroism and the rotatory dispersion have been carried out

This compound has in the visible region two adjoining optically active absorption bands which cannot be well represented by the absorption equations of Kuhn, Kuhn and Braun, Lowry and Hudson and Bielecki and Henri. So these have been represented by the empirical equation developed by the author (*this Journal*, 1947, 24, 461).

The circular dichroism of the two absorption bands are opposite in sign which has also been expressed by the empirical equations of circular dichroism (*loc. cit.*). The dissymmetry factor "g" in the two absorption bands first increases with frequency, then decreases, changes sign, again increases to a maximum and then again decreases.

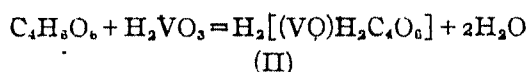
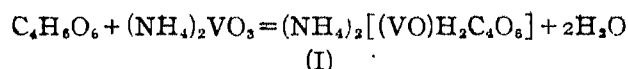
The rotatory dispersion in the region of absorption cannot be accurately expressed by the equations of Kuhn and Braun and Lowry and Hudson and has been expressed in a more satisfactory manner by means of modified equations of rotatory dispersion in the region of absorption (*loc. cit.*).

In the two preceding papers of this series (Kar, *J. Indian Chem. Soc.*, 1945, 22, 278; 1947, 24, 117) the author has reported the preparation of ammonium vanadyl *d*-tartrate and measurement of the circular dichroism and rotatory dispersion and the curves of circular dichroism and rotatory dispersion have been analysed. The investigation has now been extended to potassium vanadyl *d*-tartrate and attempts have been made to obtain more accurate results.

EXPERIMENTAL

This salt was prepared by the same method as the ammonium salt was prepared. Ammonium vanadate (meta, 1g.) was suspended in water and boiled with hydrobromic acid, when a blue solution was obtained. *d*-Tartaric acid (1.2 g.) was then added and the solution was evaporated to a small bulk. It was then neutralised with potassium hydroxide and cooled in ice when crystals of potassium vanadyl *d*-tartrate were obtained. These crystals were thoroughly washed for several times with ice-cold water and dried over calcium chloride in a vacuum desiccator. The molecular formula of the complex by Rosenheim and Mong (*Z. anorg. Chem.*, 1925, 148, 31) is $K_2[(VO)H_2C_4O_6]$.

The reactions may be represented by the following equations:—



The compounds (I) and (II) with potassium hydroxide give potassium salt.

Measurement of Rotation and Ellipticity.—Rotation and ellipticity were measured by means of Bruhat's method (*Bull. Soc. chim.*, 1930, **47**, 251). The source of light was a point —o— lite lamp of 1000 c. p. and the monochromatic radiations were obtained by passing the light through a monochromator. The extinction coefficient was determined with the help of a König-Martens spectrophotometer which was set initially at 45° .

A known strength of the solution was made in distilled water and as it was unstable in air, it was preserved in a Thunberg tube. The violet solution of the pure crystals is optically active and circularly dichroic. In the visible region it has got two optically active adjacent absorption bands. The circular dichroism of the two bands are opposite in sign so that the curve of circular dichroism cuts the axis of wave-length, while the two maxima of the two absorption bands are on the same side of the axis. The chromophoric groups, which are responsible for the two absorption bands, are under investigation.

Absorption

The extinction coefficients have been calculated by the relation $\epsilon = 2 \log \tan \theta / l$, where θ is the spectrophotometric reading and l is the length in cm., and have been tabulated in Table I and are represented graphically in Fig. 1. The molecular extinction coefficient has not been calculated as the water of crystallisation of the molecule of potassium vanadyl *d*-tartrate is not known to us. The first absorption band is reduced to a "step out", the maximum of which is very difficult to ascertain, while the second absorption band shows a maximum at about 5150\AA . Attempts have therefore been made to analyse the second absorption band only.

Analysis of the Second Absorption Curve.—The following equations have been used to analyse the absorption curve.

(a) Equation of Kuhn (*Z. physikal. Chem.*, 1929, **B4**, 14; *Trans. Faraday Soc.*, 1930, **26**, 293) namely,

$$\epsilon = \epsilon_{\max} \frac{\nu^2 \nu'^2}{(\nu_0^2 - \nu^2)^2 + \nu'^2 \nu^2} \simeq \epsilon_{\max} \frac{\nu'^2}{4(\nu_0 - \nu)^2 + \nu'^2},$$

where ϵ = extinction coefficient at frequency ν , ϵ_{\max} = maximum extinction coefficient at frequency ν_0 , ν_0 = frequency corresponding to head of the band, ν' = frequency interval between the points at which ϵ is half ϵ_{\max} which is obtained from the experimental curve of absorption.

(b) Equation of Kuhn and Braun (*Z. physikal. Chem.*, 1930, **B8**, 281) namely

$$\epsilon = \epsilon_{\max} e^{-\left(\frac{\nu_0 - \nu}{\theta}\right)^2}$$

where $\nu' = 1.6651\theta$.

(c) Equation of Lowry and Hudson (*Phil. Trans.*, 1933, **A232**, 117),

$$\epsilon = \epsilon_{\max} e^{-\left[\frac{\nu_0}{\nu} \left(\frac{\nu_0 - \nu}{\theta}\right)\right]^2}$$

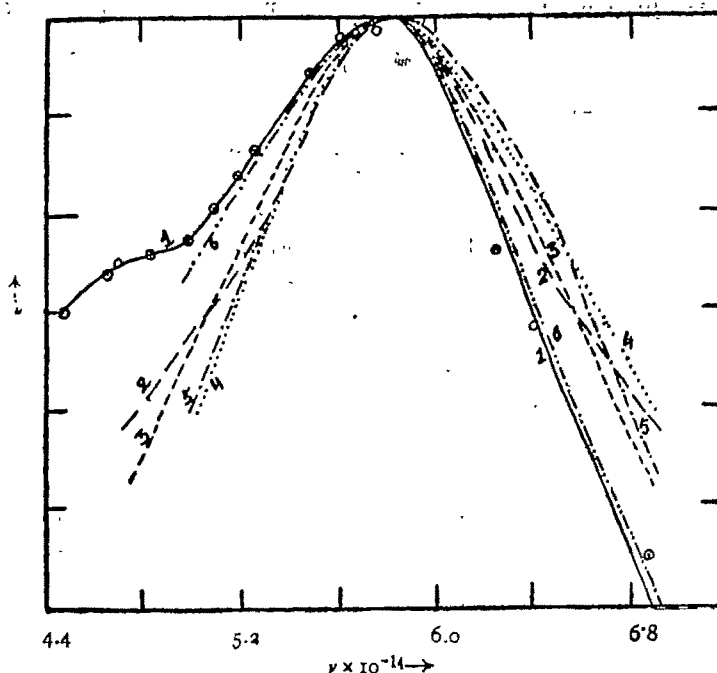
(d) Equation suggested by Bielecki and Henri (*Physikal. Z.*, 1913, **14**, 516) is

$$\epsilon = \epsilon_{\max} \frac{\nu}{\nu_0} e^{-\beta(\nu_0 - \nu)^2}$$

where $\beta = a$ constant embodying the half-width of the band. This equation differs from that proposed by Kuhn and Braun only in the insertion of the factor ν/ν_0 . The values of ϵ_{\max} , $\nu_0\nu'$ and θ , as used in the above equations, are tabulated in Table II. The extinction coefficients calculated from these four equations are tabulated in Table I and graphically represented in Fig. 1. It should be noted that none of the calculated absorption curves represent the experimental data satisfactorily where extinction coefficient is plotted against frequency.

FIG. 1

Analysis of the second absorption band of potassium vanadyl d-tartrate.



1. ———— Experimental curve.
 2. ———— Curve calculated from equation (a) of Kuhn.
 3. - - - - - Curve calculated from equation (b) of Kuhn and Braun.
 4. Curve calculated from equation (c) of Lowry and Hudson.
 5. — · — · — Curve calculated from equation (d) of Bielecki and Henri
 6. — · — · — Curve calculated from our equation

In order to represent the characteristic feature of the experimental curve the modified absorption equations (Kar, *J. Indian Chem. Soc.*, 1947, **24**, 461) have been used, namely

$$\epsilon = \epsilon_{\max} e^{-\left(\frac{\nu_0 - \nu}{\theta_1}\right)^2}$$

for extinction coefficients on the low frequency side and

$$\epsilon = \epsilon_{\max} e^{-\left(\frac{\nu - \nu_0}{\theta_2}\right)^2}$$

for extinction coefficients on the high frequency side, where the parameters θ_1 and θ_2 are defined by the following equations :

$$\theta_1 = \frac{\nu_0 - \nu_1}{0.8326} \quad \text{and} \quad \theta_2 = \frac{\nu_2 - \nu_0}{0.8326}$$

ν_1 and ν_2 are the frequencies on the long wave-length side and short wave-length side of ϵ_{\max} respectively, of the points at which ϵ is half ϵ_{\max} .

The parameters of the new equations θ_1 and θ_2 in the case of potassium vanadyl *d*-tartrate are also set out in Table II and the calculated extinction coefficients are tabulated in Table I and graphically represented in Fig. 1. It is interesting to note that the agreement between the experimental and theoretical data is now better than any of the previous equations and is well within the limits of experimental error.

TABLE I

$c = 5.625 \text{ g./100 c.c.}$ $l = 5 \text{ mm.}$ $t = 30^\circ$.

First absorption band.						
$\nu \times 10^{-14}$						
$\epsilon_{\text{obs.}}$						
	4.470	4.559	4.711	4.839	4.999	5.091
	1.209	1.365	1.406	1.447	1.488	1.618
Second absorption band.						
$\nu \times 10^{-14}$	$\epsilon_{\text{obs.}}$	$\epsilon_{\text{calc.}}$				
		(a) Kuhn	(b) K & B.	(c) L & H	(d) B & H	(e) Kar.
5.193	1.756	1.371	1.425	1.245	1.272	1.666
5.266	1.852	1.515	1.599	1.459	1.447	1.807
5.493	2.17	1.998	2.088	2.052	1.972	2.180
5.607	2.288	2.216	2.269	2.257	2.185	2.31
5.759	2.349	2.393	2.397	2.397	2.373	2.398
5.820	2.413
5.898	2.349	2.382	2.391	2.391	2.423	2.380
6.250	1.447	1.776	1.881	1.945	2.021	1.646
6.413	1.134	1.435	1.506	1.636	1.660	1.168
6.884	0.213 ?	0.757	0.5309	0.8162	0.6281	0.2339

TABLE II

Parameters of second absorption band.

λ_0	$\nu_0 \times 10^{-14}$	ϵ_{\max}	$\nu' \times 10^{-14}$	$\theta \times 10^{-14}$	$\nu_1 \times 10^{-14}$	$\theta_1 \times 10^{-14}$	$\nu_2 \times 10^{-14}$	$\theta_2 \times 10^{-14}$
5153 Å	5.82	2.41	1.44	0.865	4.96	1.033	6.4	0.6966

Circular Dichroism

Measurement of ellipticity was carried out in both the absorption bands and these were found to be opposite in sign. From the ellipticity circular dichroism was calculated by the relation

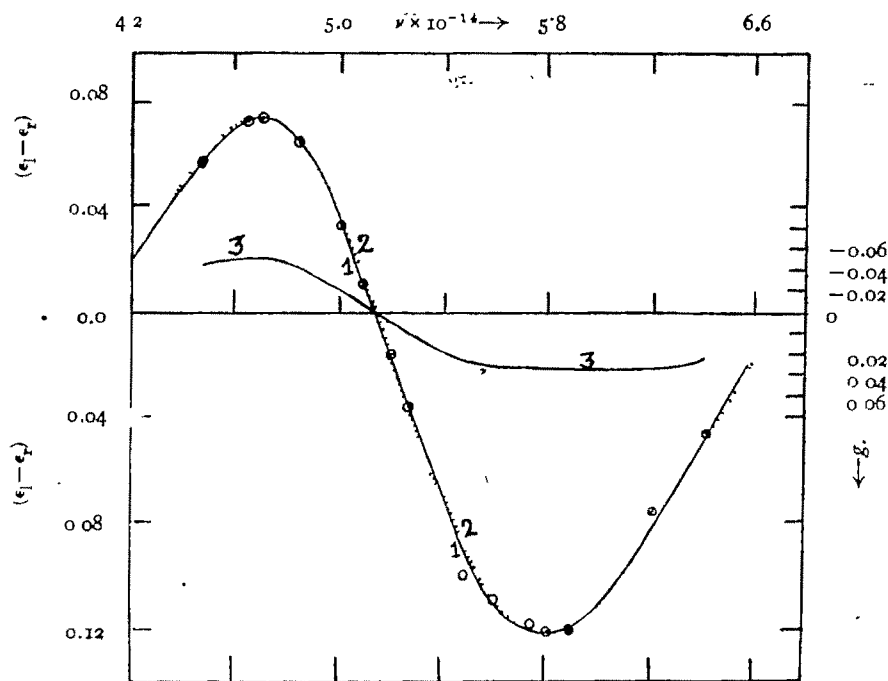
$$(\epsilon_1 - \epsilon_2) = \frac{4 \log_{10} e \phi}{l}$$

were ϵ_l and ϵ_r are the extinction coefficients for l and r light, l is the length of the solution in cm., ϕ is the ellipticity expressed in radians. If ϕ is expressed in degrees, we have

$$(\epsilon_l - \epsilon_r) = \frac{4 \times 0.4343 \times \phi}{57.296 \times l}$$

FIG. 2

Circular dichroism of potassium vanadyl d-tartrate.



1. ——— Experimental curve. 2. Theoretical circular dichroism curve.
3 Dissymmetry factor— g .

These observed values of $(\epsilon_l - \epsilon_r)$ are given in Table III against the respective frequencies. The experimental curve of circular dichroism for both the bands is represented in Fig 2. The dissymmetry factor $g = (\epsilon_l - \epsilon_r)/\epsilon$ is tabulated in Table III and is also shown in the same figure. It should be noted that the dissymmetry factor, g , first increases with increase of frequency, then decreases, changes sign and again increases to a maximum and then again decreases. The distance of separation of the two coupled electrons, according to Born's theory of electronic vibrators and Kuhn's molecular model, is also calculated by the relation

$$g_v = \frac{2\pi d}{\lambda_0} \quad \text{or} \quad d = \frac{g_v \lambda_0}{2\pi}$$

and found to be equal to 54×10^{-8} cm. in the first absorption band and 41×10^{-8} in the second absorption band.

Analysis of the Curves of Circular Dichroism.—It has already been shown that the

experimental absorption curve can be represented very closely by means of the new equations

$\epsilon = \epsilon_{\max} e^{-\left(\frac{\nu_0 - \nu}{\theta_1}\right)^2}$ for frequencies less than ν_0 and $\epsilon = \epsilon_{\max} e^{-\left(\frac{\nu - \nu_0}{\theta_2}\right)^2}$ for frequencies greater than ν_0 . Similarly, circular dichroism can also be represented to a very close approximation by the expressions

$$(\epsilon_l - \epsilon_r) = (\epsilon_l - \epsilon_r)_{\max} e^{-\left(\frac{\nu_0 - \nu}{\theta_1}\right)^2} \text{ for frequencies less than } \nu_0 \text{ and}$$

$$(\epsilon_l - \epsilon_r) = (\epsilon_l - \epsilon_r)_{\max} e^{-\left(\frac{\nu - \nu_0}{\theta_2}\right)^2} \text{ for frequencies greater than } \nu_0,$$

where ν_0 is the frequency corresponding to maximum circular dichroism $(\epsilon_l - \epsilon_r)_{\max}$ and

$\theta_1 = \frac{\nu_0 - \nu_1}{0.8320}$ and $\theta_2 = \frac{\nu_2 - \nu_0}{0.8326}$, ν_1 and ν_2 are the frequencies at which $(\epsilon_l - \epsilon_r)$ is half the

maximum value. The values of ν_0 , ν_1 , ν_2 , θ_1 , θ_2 and $(\epsilon_l - \epsilon_r)_{\max}$, as determined from the experimental curves of circular dichroism are set out in Table IV. The calculated values of $(\epsilon_l - \epsilon_r)$ according to the above equations and the corresponding curves are given side by side in Table III and in Fig. 2.

Rotatory Dispersion

This work was undertaken with the object of determining the mathematical form of the curve of rotatory dispersion in the region of absorption. The experimental data for the measurement of rotatory dispersion for a concentration of potassium vanadyl *d*-tartrate of 5.625 g./100 c.c. and length of the solution 1 cm. are given in Table V. It may be noted that the usual characteristics of anomalous rotatory dispersion associated with the first absorption band do not appear in our measurements as these all lie towards the longer wave-lengths which have not been investigated.

TABLE III

Pot. vanadyl *d*-tartrate = 5.625 g./100 c.c. $l = 1$ cm. $t = 30^\circ$.

$\nu \times 10^{-14}$	$(\epsilon_l - \epsilon_r)_{\text{obs.}}$	$(\epsilon_l - \epsilon_r)_{\text{calc.}}$	g	$\nu \times 10^{-14}$	$(\epsilon_l - \epsilon_r)_{\text{obs.}}$	$(\epsilon_l - \epsilon_r)_{\text{calc.}}$	g
First curve of circular dichroism				Second curve of circular dichroism.			
4.315	-0.038*	-0.038	...	5.193	0.0152	0.0306	0.0086
4.47	-0.0567	-0.0583	-0.0469	5.266	0.0364	0.0418	0.0196
4.659	-0.0727	-0.0748	-0.0533	5.37	0.061*	0.0609
4.711	-0.0755	-0.07598	-0.0537	5.493	0.0995	0.0835	0.0458
4.72	-0.076*	-0.076	...	5.607	0.1100	0.1059	0.0481
4.839	-0.0649	-0.066	-0.0448	5.759	0.1176	0.1211	0.0501
4.985	-0.038*	-0.038	...	5.8	0.1218*	0.1218	...
4.999	-0.03305	-0.0350	-0.0222	5.82	0.1208	0.1217	0.0501
5.091	-0.0114	-0.0195	-0.00705	5.898	0.1197	0.1191	0.05095
				6.25	0.0756	0.0753	0.0523
				6.34	0.0609*	0.0609	...
				6.413	0.047	0.0498	0.04144

* Interpolated.

TABLE IV

λ	$\nu_0 \times 10^{-14}$	$(\epsilon_1 - \epsilon_r)_{\max}$	$\nu_1 \times 10^{-14}$	$\theta_1 \times 10^{-14}$	$\nu_2 \times 10^{-14}$	$\theta_2 \times 10^{-14}$	$\theta \times 10^{-14}$
(a) Parameters of first circular dichroism curve							
5356Å	4.72	-0.075	4.315	0.4865	4.985	0.3183	0.4024
(b) Parameters of second circular dichroism curve.							
5172Å	5.8	0.1218	5.37	0.5165	6.34	0.6486	0.5826

These observed rotations for each wave-length, $[\alpha]$, are the algebraic sum of all the partial rotations due to different optically active absorption bands in the visible and ultraviolet regions. These observed values of rotations are represented graphically as curve 1 in Fig. 3.

Analysis of the Curve of Rotatory Dispersion.—The following equations have been used to analyse the curve of rotatory dispersion.

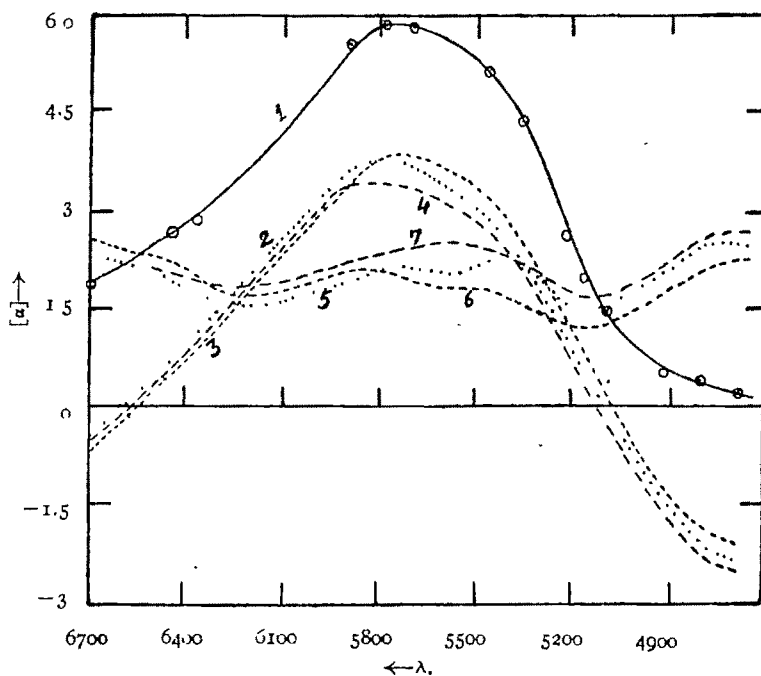
(a) Equation of Kuhn and Braun (*loc. cit.*), namely

$$\alpha = \frac{57.3}{2\sqrt{\pi}} \cdot \frac{(\epsilon_1 - \epsilon_r)_{\max}}{\log_{10} e} \cdot \frac{\nu}{\nu_0} \left[e^{-\left(\frac{\nu_0 - \nu}{\theta}\right)^2} \int_0^{\frac{\nu_0 - \nu}{\theta}} e^{-x^2} dx - \frac{\theta}{2(\nu_0 + \nu)} \right]$$

where α is the rotatory contribution of an optically active absorption band, expressed in degrees per cm. column of the solution at frequency ν ; ϵ_1, ϵ_r are the extinction coefficients of l and r light and $(\epsilon_1 - \epsilon_r)_{\max}$ is the maximum value of the circular dichroism of that band at frequency ν_0 and the parameter θ is related to the half-width of the experimental curve of circular dichroism of the band by the relation $\nu' = 1.6651\theta$. The values of $(\epsilon_1 - \epsilon_r)_{\max}$, ν_0 and θ for both the curves of circular dichroism are already given in Table IV. The rotatory contributions at different wave-lengths for each of the absorption bands have been calculated separately.

The algebraic sum of the calculated partial rotations, $[\alpha]_1$ and $[\alpha]_2$, for different wave-lengths of the two optically active absorption bands and the difference between $[\alpha]$ and $[\alpha]_1 + [\alpha]_2$ are given in Table V. This difference evidently represents the residual rotations due to absorption bands in the ultraviolet region. The algebraic sum of the calculated partial rotations and also the residual rotation are represented graphically as curves 2 and 5 in Fig. 3. The difference curve 5 should be normal, that is, the rotation should increase progressively with decreasing wave-lengths in the region of the first and the second absorption bands; but it actually contains two loops, one in the region of first absorption band and the other in the region of second absorption band. These loops may be attributed partly to experimental errors and partly to the fact that the absorption equation of Kuhn and Braun, on the basis of which the above rotation equation has been derived, could not represent the experimental data accurately.

FIG. 3

Rotatory dispersion of potassium vanadyl d-tartrate.

1. Experimental curve.
2. Theoretical curve calculated from the equation of Kuhn and Braun
3. Theoretical curve calculated from the equation of Lowry and Hudson
4. Theoretical curve calculated from our equation.
5. Difference curve (curve 1 minus curve 2).
6. Difference curve (curve 1 minus curve 3).
7. Difference curve (curve 1 minus curve 4)

(b) Equation of Lowry and Hudson, namely

$$\alpha = \frac{57.3}{2\sqrt{\pi}} \cdot \frac{(\epsilon_l - \epsilon_r)_{\max}}{\log_{10} e} \cdot \frac{\lambda_0}{\lambda} \left[e^{-\left(\frac{\lambda - \lambda_0}{\theta}\right)^2} \int_0^{\frac{\lambda - \lambda_0}{\theta}} e^{x^2} dx + \frac{\theta}{2(\lambda + \lambda_0)} \right]$$

$$= \frac{57.3}{2\sqrt{\pi}} \cdot \frac{(\epsilon_l - \epsilon_r)_{\max}}{\log_{10} e} \cdot \frac{\nu}{\nu_0} \left[e^{-\left[\frac{\nu_0}{\nu} \left(\frac{\nu_0 - \nu}{\theta}\right)\right]^2} \int_0^{\frac{\nu_0}{\nu} \left(\frac{\nu_0 - \nu}{\theta}\right)} e^{x^2} dx + \frac{\nu \theta}{2\nu_0(\nu_0 + \nu)} \right]$$

The symbols have the same significance and values as before. The algebraic sum of the calculated partial rotations $[\alpha]_1$ and $[\alpha]_2$ and the difference between the observed rotation and this algebraic sum are tabulated in Table V. The algebraic sum of the calculated partial rotations and also the difference are also represented graphically as curve 3 and 6 in Fig. 3. The difference curve 6 shows that the two loops, one in the first absorption

band and the other in the second absorption band, shows no sign of improvement towards disappearance, thus indicating that the absorption equation of Lowry and Hudson, on which the above rotation equation is based, is also inadequate to represent the experimental data accurately.

(c) A third attempt was made to analyse the curve of rotatory dispersion by means of a modified expressions of the same type as that of Kuhn and Braun, based on our new absorption equations and already given in the preceding paper (*loc. cit.*). The equations are

$$\alpha = \frac{57.3}{2\sqrt{\pi}} \cdot \frac{(\epsilon_l - \epsilon_r)_{\max}}{\log_{10} e} \cdot \frac{\nu}{\nu_0} \left[e^{-\left(\frac{\nu_0 - \nu}{\theta_1}\right)^2} \int_0^{\frac{\nu_0 - \nu}{\theta_1}} e^{x^2} dx - \frac{\theta_1}{2(\nu_0 + \nu)} \right]$$

for frequencies less than ν_0 , and

$$\alpha = -\frac{57.3}{2\sqrt{\pi}} \cdot \frac{(\epsilon_l - \epsilon_r)_{\max}}{\log_{10} e} \cdot \frac{\nu}{\nu_0} \left[e^{-\left(\frac{\nu - \nu_0}{\theta_2}\right)^2} \int_0^{\frac{\nu - \nu_0}{\theta_2}} e^{x^2} dx + \frac{\theta_2}{2(\nu_0 + \nu)} \right]$$

for frequencies greater than ν_0 .

TABLE V

Conc. of pot. vanadyl *d*-tartrate = 5.625 g./100 c.c. $l = 1$ cm. $t = 30^\circ$. Observed rotation = $[\alpha] = X$. Algebraic sum of the calculated partial rotation according to different equations = $[\alpha]_1 + [\alpha]_2 = Y$.

λ	Kuhn & Braun			Lowry & Hudson		Kar	
	X.	Y.	X - Y.	Y.	X - Y.	Y.	X - Y.
6708Å	1.87	-0.44	2.31	-0.67	2.54	-0.42	2.29
6438	2.66	0.67	1.99	0.44	2.22	0.60	2.06
6362	2.87	1.12	1.75	0.88	1.99	0.96	1.91
5893	5.58	3.61	1.97	3.49	2.09	3.38	2.20
5780	5.85	3.71	2.14	3.76	2.09	3.39	2.46
5700	5.80	3.65	2.15	3.83	1.97	3.31	2.49
5461	5.10	2.89	2.21	3.25	1.85	2.74	2.36
5350	4.30	2.16	2.14	2.53	1.77	2.09	2.21
5209	2.60	1.01	1.59	1.35	1.25	0.83	1.77
5153	1.97	0.49	1.48	0.78	1.19	0.28	1.69
5086	1.47	-0.15	1.62	0.15	1.32	-0.28	1.75
4800	0.38	-2.13	2.51	-1.77	2.15	-2.18	2.56
4678	0.25	-2.26	2.51	-2.01	2.26	-2.42	2.67

θ_1 and θ_2 for both the bands have the same values as used in our circular dichroism equations and given in Table IV and the other symbols have the same significance and values as before. The algebraic sum of the calculated partial rotations and the difference between the observed rotation and this sum are also given in Table V and represented graphically as curves 4 and 7 in Fig. 3. The difference curve 7 shows that the two loops, which has to be eliminated, show a sign of improvement, though not disappeared, thus indicating that the above expressions represent the partial rotations of both the bands more accurately than the equation of Kuhn and Braun and of Lowry and Hudson.

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DEPARTMENT OF PHYSICAL CHEMISTRY,
UNIVERSITY OF DACCA

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SEARCH FOR INSECTICIDES. PART I

By A. B. SEN AND P. M. BHARGAVA

Preparation of certain trichloro-2-hydroxy-2-halogenated phenylethanes and halogenated phenyl esters of trichloroacetic acid has been described.

Two theories have been put forward concerning the remarkable insecticidal powers of dichlorodiphenyltrichloroethane (Busvine, *Nature*, 1945, **156**, 169). One postulates that toxic component is the linked *p*-chlorobenzene rings, while the chloroformic residue $-CCl_3$ imparts lipid solubility (Läuger, Martin and Müller, *Helv. Chim. Acta*, 1944, **27**, 892). According to the other theory, the lipid solubility is attributed to the chlorobenzene rings, while the remainder of the molecule is supposed to be responsible for toxicity, by splitting off HCl at the vital centres (Martin and Wain, *Nature*, 1944, **154**, 512).

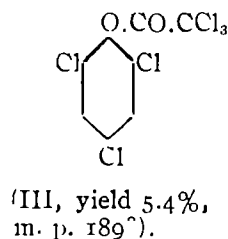
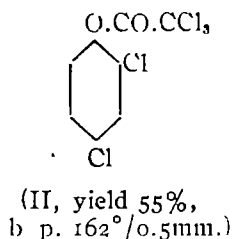
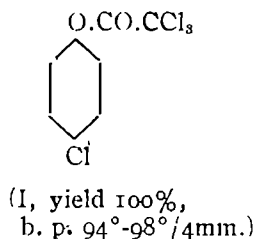
In this paper, two types of reactions have been carried out in order to introduce a toxic and a lipid soluble group in the molecule, with a view to studying the effect of these different groups on insecticidal action.

The first is the condensation of chloral with the Grignard reagents of polyhalogenated benzenes. Condensation of chloral with Grignard reagents of *p*-chlorobromobenzene, *o*-chlorobromobenzene and 1:2-dichloro-4-bromobenzene yields 1:1:1-trichloro-2-hydroxy-2-(4-chlorophenyl)ethane, 1:1:1-trichloro-2-hydroxy-2-(2-chlorophenyl)ethane and 1:1:1-trichloro-2-hydroxy-2-(3:4-dichlorophenyl)ethane respectively. Of these compounds, the first [*i. e.* 1:1:1-trichloro-2-hydroxy-2-(4-chlorophenyl)ethane] has been obtained previously, as a by-product in the manufacture of DDT (Forest, Stephenson and Waters, *J. Chem. Soc.*, 1946, 333). According to them, the compound is contained in the lower boiling fraction (b. p. 115°/0.5 mm.) which is obtained as a by-product in the technical preparation of DDT, and that the compound yields an acetyl derivative which on hydrolysis regenerates the original hydroxy compound as a solid. The present authors have obtained 1:1:1-trichloro-2-hydroxy-2-(4-chlorophenyl)ethane as a viscous liquid, b. p. 196°-198°/11 mm. It yields an acetyl derivative which is not hydrolysed by *N*/2-sulphuric acid. 1:1:1-Trichloro-2-hydroxy-2-(2-chlorophenyl)ethane also yields an acetyl derivative, but the acetyl derivative of 1:1:1-trichloro-2-hydroxy-2-(3:4-dichlorophenyl)ethane could not be obtained.

It has been incidentally found that the bromination of chlorobenzene in CCl_4 solution, in the presence of Al-Hg couple, results in the formation of *p*-chlorobromobenzene in a good yield, whereas if the same reaction is carried out without a solvent, the reaction is much more vigorous and the product formed is mainly the isomeric *o*-chlorobromobenzene.

Another series of compounds, which have been prepared, is of the type of esters. These have been obtained by the condensation of the sodium salts of *p*-chlorophenol, 2:4-dichlorophenol and 2:4:6-trichlorophenol with trichloroacetyl chloride. *p*-Chlorophenol gives a theoretical yield of the trichloroacetyl ester (I). 2:4-Dichlorophenol, which has

one *ortho* position occupied by chlorine, gives a 55% yield of the ester (II), while in the case of 2:4:6-trichlorophenol, which has both the *ortho* positions substituted, the yield of the trichloroacetyl ester (III) is very low (5.4%).



EXPERIMENTAL

p-Chlorobromobenzene was obtained by Korner previously by the bromination of chlorobenzene (*Gazzetta*, 1874, 4, 342; "Jahresbericht uber die Fortschritter der Chemie," 1875, p. 319), but the exact experimental details not being available it was prepared by the authors in the following way.

The bromination was carried out in a 500 c. c. welded-neck flask, fitted with a dropping funnel and a reflux condenser, connected at the top to a gas absorption trap. Chlorobenzene (40 g.), diluted with an equal volume of CCl_4 , was taken in the flask, and a little freshly prepared Al-Hg couple added to it. Bromine (20 c. c.) was then added dropwise through the dropping funnel, in the course of 1½ hours, the flask being surrounded by ice-water, and the contents of the flask were left at room temperature overnight. Next day, on diluting with alcohol (100 c. c.), orange-yellow plates of *para*-chlorobromobenzene separated out. The crystals were filtered off at the pump. On removing the alcohol from the filtrate and cooling, another crop of the compound was obtained, yield 40 g. (59% of theory), m. p. 66°.

1:1:1-Trichloro-2-hydroxy-2-(4-chlorophenyl)ethane.—The Grignard reagent was prepared by adding *p*-chlorobromobenzene (17 g.), dissolved in ether, to magnesium (2.3 g.) suspended in ether (50 c. c.), under continuous stirring by a mechanical stirrer in an atmosphere of nitrogen, and refluxing for about 2 hours. The dark coloured solution was then cooled in ice and chloral (13 g.), diluted with an equal volume of ether, added to it drop by drop during the course of an hour, when a yellow product separated out. The mixture was then refluxed for an hour, the Grignard complex acidified with dilute sulphuric acid and then transferred to a separating funnel. The deep yellow, emulsion-like ethereal layer was separated, washed with sulphuric acid and then with water till free from acid. It was left in a refrigerator for 48 hours and then filtered. A yellowish residue (1 g.) which did not melt and which was insoluble in ether, was left and could not be identified. The filtrate was dried over anhydrous sodium sulphate and the ether distilled off on a water-bath, final traces being removed at the water pump. The residual liquid was then distilled in vacuum on a metal bath, when a bright yellow, very viscous liquid was obtained at 194°-198°/11 mm. The liquid possesses a characteristic smell and reacts with sodium, yield 13 g. (55% of theory). (Found: C, 36.66; H, 2.28; Cl, 54.29. $\text{C}_8\text{H}_6\text{OCl}_4$ requires C, 36.92; H, 2.31; Cl, 54.61 per cent).

The *acetyl derivative* of the above was prepared by boiling the hydroxy compound with acetic anhydride and anhydrous sodium acetate for 5 minutes, and then allowing it to cool. The mixture was then diluted with water and boiled to decompose the excess of acetic anhydride. On cooling, the acetyl derivative was precipitated (theoretical yield). Recrystallised from dilute acetic acid, it was obtained as fine, white needles, m. p. 118-119°. (Found: C, 39.31; H, 2.62. $C_{10}H_5O_2Cl$ requires C, 39.73; H, 2.65 per cent).

o-Chlorobromobenzene.—Bromination of chlorobenzene (15 g.) was carried out in the same way as in the preparation of the *p*-isomer, excepting that the chlorobenzene was not diluted with CCl_4 . The reaction was much more vigorous. After the addition of bromine, the mixture was left for a week for the completion of the reaction, then treated with a solution of sodium bicarbonate to remove HBr and Br_2 , and the oil separating was taken up with ether. The ethereal extract was filtered and the filtrate left for evaporation of the ether at the room temperature. The residual oil was distilled under ordinary pressure, when at 196°-200° a colourless liquid was obtained. This on cooling in ice deposited a few crystals of *p*-chlorobromobenzene. The supernatant liquid was decanted off and redistilled, b. p. 196°-199°, yield 14.5 g. (58% of theory). (Found: C, 37.97; H, 2.07. Calc for C_6H_4ClBr : C, 38.12; H, 2.14 per cent).

1:1:1-Trichloro-2-hydroxy-2-(2-chlorophenyl)ethane.—The Grignard reagent was prepared by adding *o*-chlorobromobenzene (12.8 g.) in ethereal solution to magnesium (22 g.), suspended in ether (50 c.c.), under continuous stirring by a mechanical stirrer in an atmosphere of nitrogen, and refluxing for about 4 hours. The dark coloured solution was then cooled in ice, and chloral (9.9 g.), diluted with an equal volume of ether was added drop by drop during the course of an hour; it was then worked up in a similar manner as with the -2-(4-chlorophenyl)ethane analogue. An insoluble residue, which did not melt, was obtained in this experiment also. The filtered ethereal extract was dried over anhydrous sodium sulphate and the ether distilled off on a water-bath. The residual liquid was distilled in vacuum on a metal-bath, when a brilliant red, viscous liquid collected in the receiver at 196°-198°/7mm. The liquid possesses a characteristic smell and reacts vigorously with sodium, yield 8 g. (46% of theory). (Found: C, 36.49; H, 2.07; Cl, 54.91. $C_8H_6OCl_4$ requires C, 36.92; H, 2.31; Cl, 54.61 per cent).

The *acetyl derivative* of the above compound was prepared in the usual way (theoretical yield). Recrystallisation from dilute acetic acid gave a colourless crystalline compound, m. p. 96-97°. (Found: C, 39.25; H, 2.72. $C_{10}H_5O_2Cl$ requires C, 39.73; H, 2.75 per cent).

1:1:1-Trichloro-2-hydroxy-2-(3:4-dichlorophenyl)ethane.—The Grignard reagent of 1:2-dichloro-4-bromobenzene (18.5 g., b. p. 124°/33mm.) with Mg (2.3 g.) was prepared in a similar way as described in the preceding compound with about 6 hours' refluxing. The solution was then cooled in ice and reacted with chloral (13.5 g.), and the yellow mixture was then refluxed for an hour; the Grignard reagent was then decomposed and extracted as in the case of -2(4-chlorophenyl) ethane. The ethereal extract after washing was dried over anhydrous sodium sulphate, filtered and the ether distilled off,

final traces being removed on a water pump. The residual liquid was then distilled in vacuum on a water-bath, when a bright orange-red liquid was obtained at 55° - $57^{\circ}/5\text{mm.}$ It solidified on cooling in ice to a red crystalline solid, having a characteristic smell and reacting vigorously with sodium, yield 10 g. (42% of theory). (Found: C, 32.20; H, 1.82; Cl, 59.93. $\text{C}_6\text{H}_5\text{OCl}_3$ requires C, 32.70; H, 1.70; Cl, 60.27 per cent). The colour of the liquid faded on keeping and in the course of a few months it disappeared completely, a crystalline colourless solid being then obtained on cooling in ice.

Trichloroacetate of p-Chlorophenol.—The sodium salt of *p*-chlorophenol was prepared by adding a little less than the required amount of caustic soda, dissolved in a small quantity of water, to the phenol, using phenolphthalein as the indicator. The solution was evaporated to dryness on a water-bath and left in a vacuum desiccator.

The sodium salt of *p*-chlorophenol (7.5 g.) was suspended in petrol ether (50 c.c.) in a pyrex flask fitted with a reflux condenser and trichloroacetyl chloride (10.5 g., slight excess over the required amount) was added. A vigorous reaction with brisk effervescence ensued. After the reaction had subsided, the mixture was refluxed on a water-bath for $\frac{3}{4}$ hour, when the petrol ether layer assumed a dark green colour, with the separation of sodium chloride. The reaction mixture was cooled and then filtered. The petrol ether was distilled off from the filtrate on a water-bath, final traces of the solvent being removed on a water pump. The residual liquid was then distilled in vacuum on an oil-bath, when a colourless liquid, b. p. 94° - $98^{\circ}/4\text{mm.}$, was obtained, yield theoretical. The liquid possesses a characteristic smell and darkens on keeping. (Found: C, 34.81; H, 1.66; Cl, 51.52. $\text{C}_6\text{H}_4\text{O}_2\text{Cl}_4$ requires C, 35.03; H, 1.46; Cl, 51.82 per cent).

The ester on hydrolysis with 20% alcoholic potash regenerated *p*-chlorophenol and trichloroacetic acid. The hydrolysis was carried out by refluxing for $1\frac{1}{2}$ hours the ester (2 g.) with 20% alcoholic potash (30 c.c.) to which water (2 c.c.) was added. After hydrolysis, the alcohol was removed by distillation, the residue was cooled in ice and then acidified with 18% hydrochloric acid, when crystals of trichloroacetic acid separated out and *p*-chlorophenol was obtained as a red oil forming a layer. The chlorophenol was separated by extraction with ether; the ethereal extract was washed with sodium bicarbonate solution, and the phenol then identified after distillation, b. p. 215° .

Trichloroacetate of 2:4-Dichlorophenol.—The dry sodium salt of dichlorophenol (10.2 g.), prepared in the same way as in the previous experiment, was suspended in petrol ether (50 c.c.) and trichloroacetyl chloride (20 g., approximately double the theoretical amount) added to it. After the vigour of the reaction had subsided, the mixture was refluxed for $\frac{3}{4}$ hour, cooled and then filtered. The filtrate was washed with 1% caustic soda solution, and then with water till free from alkali. It was dried over anhydrous sodium sulphate and the petrol ether distilled off on a water-bath. Trichloroacetyl chloride and last traces of the solvent were removed on a water pump and the residual liquid distilled in vacuum on a metal bath. The first fraction (boiling between 80° and $130^{\circ}/0.5\text{ mm.}$) consisted mainly of the unchanged dichlorophenol (4 g. approximately) which solidified in the receiver, and was collected separately. The ester distilled at $162^{\circ}/0.5\text{ mm.}$ or $167^{\circ}/3\text{ mm.}$ as a colourless liquid which did not solidify in the receiver. The liquid possesses a pungent smell and acquires a dark brown colour in course of time, yield 8.4 g. (55% of theory).

(Found: C, 31.22; H, 1.11; Cl, 57.99. $C_8H_3O_2Cl_5$ requires C, 31.44; H, 0.97; Cl, 57.54 per cent).

Trichloroacetate of 2:4:6-Trichlorophenol.—The sodium salt of 2:4:6-trichlorophenol was prepared in the same way as the sodium salt of *p*-chlorophenol. Trichloroacetyl chloride (10 g., approximately double the theoretical amount) was then added to dry sodium salt of the trichlorophenol (12 g.) in petrol ether. The mixture was refluxed for $\frac{3}{4}$ hour and left overnight. It was then filtered and solvent distilled off. Trichloroacetyl chloride and the last traces of the solvent were removed on a water pump. The residual liquid was then distilled in vacuum on a metal-bath, when at $83^\circ/1$ mm., the unchanged trichlorophenol collected and solidified in the receiver. About 85% of the trichlorophenol was thus recovered back. After no more of the phenol distilled, the residue in the Claisen flask was washed several times with 2% sodium hydroxide solution. The insoluble portion, covered with the alkali solution, was left in a refrigerator and filtered the next day. The residue was washed with about 20 c.c. of petrol ether and then dried. The ester was thus obtained as a dull, white, crystalline solid, m. p. 189° , yield 1.2 g. (5.4% of theory). (Found: C, 27.47; H, 0.70. $C_8H_4O_2Cl_3$ requires C, 28.0; H, 0.58 per cent).

The insecticidal action and some physical properties of the compounds, described above, are under investigation.

One of the authors (P. M. B.) is indebted to the Lucknow University for the award of a research grant, and to the U. P. Government for the award of a research scholarship for continuing this work.

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LUCKNOW UNIVERSITY.

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SYNTHESIS OF SUBSTITUTED DINITRO PHENYLKETONES AND PHENYLACETIC ACIDS. PART III.

By A. B. SEN AND P. M. BHARGAVA

2:4-Dinitro-6-iodophenylacetone and 2:4-dinitro-6-iodophenylacetic acid have been prepared by the ketonic and acid hydrolysis respectively, of 2:4-dinitro-6-iodophenylacetoacetic ester. 2-Methyl 3-ethylcarboxy-5-iodo-7-aminoindole has been obtained by the reduction of the above mentioned ester with iron powder and water.

In the previous communications of this series (this *Journal*, 1947, **24**, 268, 371) it has been shown that 1-chloro-2:6-dinitro-4-bromobenzene and 1-chloro-2:4-dinitro-6-bromobenzene condense easily with acetoacetic and malonic esters in absolute ether, and the condensation products, so obtained, yield the respective dinitrobromophenylacetic acids and acetones on hydrolysis with alkali and acid respectively.

In this paper this reaction has been extended to 1-chloro-2:4-dinitro-6-iodobenzene.

EXPERIMENTAL

2:4-Dinitro-6-iodophenol was prepared previously by Armstrong (*Ber.*, 1873, **6**, 651) by the iodination of 2:4-dinitrophenol, but the exact experimental details are not available. It was therefore prepared by dissolving 2:4-dinitrophenol (36.8 g.) in hot glacial acetic acid and adding to it gradually a finely powdered mixture of iodine (40.8 g.) and freshly precipitated yellow mercuric oxide (21.7 g.) during the course of 6 hours. Each addition of the mixture was followed by heating to boiling and stirring by a mechanical stirrer till the colour of the iodine was discharged. Afterwards, it was finally stirred for an hour and the precipitated mercuric iodide allowed to settle down. The acetic acid layer was decanted off and diluted with water; the reddish yellow product was filtered and recrystallised from hot alcohol when fine yellow needles were obtained, m.p. 102°, yield 42 g. A further quantity (12 g.) was obtained from the filtrate by removal of the alcohol, yield 87.1% of theory. One more recrystallisation raised the melting point to 106° (cf. Armstrong, *loc. cit.*), but for the preparation of the chlorodinitroiodobenzene this is not necessary.

1-Chloro-2:4-dinitro-6-iodobenzene was prepared from 2:4-dinitro-6-iodophenol (40 g.), *p*-toluene sulphonyl chloride (27.4 g.) and diethylaniline (20 c.c.) by the method of Joshi and Sane (*J. Indian Chem. Soc.*, 1932, **9**, 60) with a slight modification. The mixture, after heating on a water-bath for 4 hours, was treated with dilute hydrochloric acid, when an oil separated out. The hydrochloric acid layer was decanted off and the oil treated with a small quantity of alcohol when in a short time it solidified. On filtration the chloro compound was obtained in the form of greenish yellow needles, m.p. 102°, yield 30 g. (70.8% of theory). Recrystallisation from hot alcohol raised the melting point to 106° (cf. Armstrong, *loc. cit.*); for condensation with acetoacetic ester the crude product was used.

4-Dinitro-6-iodophenylacetoacetic Ester.—The sodium derivative of ethyl acetoacetate was prepared from 20.8 g. of ethyl acetoacetate and 3.7 g. of sodium in 40 c.c. of ether. When the last traces of sodium had disappeared, the solution was cooled in ice and 1-chloro-2,4-dinitro-6-iodobenzene (26.4 g.) was added. The mixture was refluxed for 6 hours and then left overnight. It was extracted first with water (300 c.c. approx.) and then with equal amount of 2% caustic soda solution, and the combined extracts acidified with dilute nitric acid, when a dark coloured oil separated out. After standing overnight in a refrigerator, the supernatant aqueous layer was decanted off, the oil dissolved in cold alcohol and the alcoholic solution allowed to evaporate slowly, when the ester crystallised out as dark coloured plates. Crops were collected after a week, but after about 19 g. had been collected, further evaporation of the alcoholic solution yielded only an oil. Recrystallisation was effected by dissolving in cold alcohol, filtering, and allowing it to evaporate by itself, when dark reddish brown crystals of the ester were obtained, m.p. 74° , yield 57.4% of theory. (Found: N, 6.80. $C_{12}H_{11}O_7N_2I$ requires N, 6.61 per cent).

The reaction was also carried out in anhydrous benzene instead of ether, and the same yield of the ester was obtained.

2:4-Dinitro-6-iodophenylacetone.—The finely powdered crude ester (5.8 g.) was dissolved in concentrated sulphuric acid (51 c.c.) and water (24 c.c.) added without cooling. After the evolution of carbon dioxide had ceased, the dark solution was poured on crushed ice, allowed to stand in a refrigerator for 2 days and then filtered. The product was dissolved in hot alcohol, filtered and the filtrate allowed to evaporate slowly, when the ketone crystallised out as dark coloured needles, m.p. 110° , yield 4 g. (83.1% of theory). (Found: N, 8.11. $C_8H_5O_2N_2I$ requires N, 8.0 per cent).

The *phenylhydrazone* was prepared by dissolving the above ketone (1 g.) in the minimum quantity of alcohol and adding to it about 1.5 c.c. of phenylhydrazine. The mixture was refluxed for half an hour and then cooled. The phenylhydrazone separating was filtered and recrystallised from hot alcohol as light, fine red flakes, m.p. 74° (decomp.), yield 1.0 g. (79.6% of theory). (Found: N, 12.91. $C_{10}H_{13}O_2N_2I$ requires N, 12.73 per cent).

The *oxime* was obtained by dissolving the above ketone (1.2 g.) in alcohol and adding to it hydroxylamine hydrochloride (0.6 g.) followed by caustic soda solution, till it turned just alkaline to phenolphthalein. After refluxing the mixture for an hour, the contents were poured in 100 c.c. of water, allowed to stand for 2 days in a refrigerator and then filtered. The dark coloured product was dissolved in hot alcohol, filtered, and the filtrate allowed to evaporate, when the oxime crystallised out as fine needles, m.p. 75° , yield 0.8 g. (64% of theory). (Found: N, 11.07. $C_8H_8O_2N_2I$ requires N, 11.38 per cent).

2:4-Dinitro-6-iodophenylacetic Acid.—The crude 2:4-dinitro-6-iodophenylacetoacetic ester (3 g.) was refluxed for half an hour with 15 c.c. of 20% alcoholic potash to which 1 c.c. of water had been added. The alcohol was then distilled off, the residue acidified with dilute hydrochloric acid, left overnight and then filtered. The filtrate was allowed to evaporate slowly when the acid crystallised out as a dark brown powder.

It does not melt, but on heating strongly gives off iodine. It dissolves in sodium bicarbonate solution with effervescence and is reprecipitated by hydrochloric acid as a brown powder, confirming that it is an acid; yield 2 g. (80% of theory). (Found: N, 7.58. $C_8H_5O_6N_2I$ requires N, 7.95 per cent).

2-Methyl-3-carboxyethyl-5-iodo-7-aminoindole.—The crude 2:4-dinitro-6-iodo-phenylacetoacetic ester (2 g.), iron powder (3 g.), crystallised ferrous sulphate (0.3 g.) and water (10 c.c.) were refluxed for 3 hours and then cooled in ice-water with constant shaking. After filtration, the residue was boiled with alcohol (20 c.c.) and animal charcoal and the extract filtered hot. The filtrate was allowed to evaporate slowly, when the cyclised amine crystallised out as a colourless solid, which turned black immediately on exposure to atmosphere, m.p. 135° (decomp.), yield 1.2 g. (73.6% of theory). (Found: N, 8.25. $C_{12}H_{13}O_2N_2I$ requires N, 8.14 per cent).

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STUDIES ON THE DIELECTRIC POLARISATION AND THE DIPOLE MOMENTS OF ENANTIOMERS

BY ROOP CHAND SAHNEY, MISS ROSHAN BARUCHA AND H. R. SARNA*

Dielectric polarisations and dipole moments of *d*, *l* and *dl* forms of camphor, borneol and menthol at different concentrations have been determined to adduce support for the Pasteur's principle of molecular dissymmetry and to investigate the nature of linkage in *dl* compounds

B. K. Singh and collaborators (*Curr. Sci.*, 1933, 3, 420; *Proc. Ind. Acad. Sci.*, 1935, 2A, 378 *et seq*) have shown from the studies of the values of viscosity, density and refractive index for solutions of *d*, *l* and racemic forms that the values were identical up to certain concentrations only and that at higher concentrations though the values for *d* and *l* forms agreed, as is to be expected from the Pasteur's principle of molecular dissymmetry, the values for the racemic forms were apparently higher than the corresponding values for the active enantiomers. It was thus concluded that at higher concentrations the racemic forms were present as equimolecular compound of enantiomers.

In view of the above it was thought instructive to investigate the total polarisations and dipole moments of the enantiomers at different concentrations to see if further support could be obtained for Pasteur's principle of molecular dissymmetry and to investigate the nature of linkage present in the *dl* compounds.

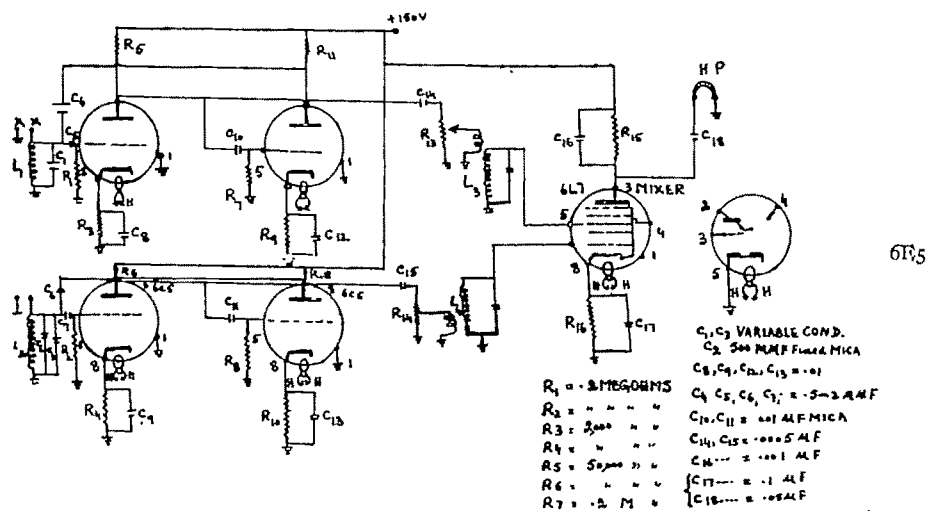
EXPERIMENTAL

Substances used in the present investigation were freshly prepared, specially purified, and their melting points and rotatory powers were determined before the measurements of dielectric constant were made on them. The determinations of the dielectric constant were carried out in specially purified and recrystallised benzene by the heterodyne beat apparatus. The apparatus consists of two high frequency oscillatory circuits the output from which are electrically mixed to produce the beat frequency, which is amplified and detected with head-phones and a magic eye detector. A brief sketch of the apparatus is shown in Fig. 1.

In this diagram the two upper left 6c5 triodes are connected as a Franklin oscillator, which is well known for its high frequency stability approaching that of a crystal oscillator. Similarly the two lower left 6c5 tubes make up another such oscillator. L_1C_1 and L_2C_2 are the oscillatory circuits, and out of these components, C_2 is a precision standard calibrated condenser. C_3 is the test condenser, which is connected in parallel with C_2 with short, stiff wires, and the capacity of the test condenser becomes measured by the adjustment of C_2 to get zero beat in each case. C_4 , C_5 , C_6 and C_7 are very small adjustable capacities of values about 2 to 3 $\mu\mu\text{F}$. The output from the two Franklin oscillators is filtered at L_3 and L_4 and then subjected to electronic mixing in the

* The address of the authors has changed since partition of Punjab to the East Punjab University, Simla.

FIG. 1



The number of the two upper left triodes is 6E5 The one next to the extreme right (6E5) is to be read as 6E5b₁

pentagrid converter, 6L7. The absence of pulling between the two circuits was shown by the fact that zero beat, once it was adjusted, would remain unaltered for hours together. In fact, it was found that after the circuit had been adjusted for zero beat and then turned off, when it was turned on again on the next day, the adjustment was still perfect. The plate of 6L7 is connected to the grid (3) of the magic eye detector (6E5) and by this means the conditions of zero beat can be tested both visually and aurally. Near about the position the fluorescent cone begins to flicker, and at the correct position the flicker disappears, and there is a perfect silence in phones. We found the apparatus, which was assembled in the laboratory, highly satisfactory and sensitive.

Table I records the dipole moments of these sets of compounds and Table II shows the total polarisations of these and those of the camphorquinone at different concentrations.

TABLE I

Melting point and dipole moments of the enantiomers at 20°-21°.

Subs.	M p.	¹ Dip. mom $\mu \times 10^{18}$.	Subs.	M.p	¹ Dip mom $\mu \times 10^{18}$.	Subs.	M p	¹ Dip mom $\mu \times 10^{18}$.
d-Camphor	176°	2.90	d-Borneol	208°	1.6	d-Menthol	39°	1.54
l-Camphor	178.5	2.905	l-Borneol	206	1.59	l-Menthol	43	1.54
dl-Camphor	179	2.91	dl-Borneol	210.5	1.59	dl-Menthol	34	1.55

* Expressed in Debye unit

The experimental error in the determination of the dipole moments is of the order 0.05 to 1%.

TABLE II

Total polarisation values at different concentrations at 20°.

Substances.	Concentration (in g./100 c.c. of benzene).					
	1%.	2%.	5%.	10%.	12%.	14%.
<i>d</i> -Camphor	235	235	233	230	228	226
<i>l</i> - "	235	235	232.5	230	228.5	222
<i>dl</i> - "	235	235	232	228	226	223
<i>d</i> -Borneol	102	102	99	97	94	92
<i>l</i> - "	102	102	98.5	97	94	91.5
<i>dl</i> - "	102	102	97	95	91	89
<i>d</i> -Menthol	105	105	104	102	100	98
<i>l</i> - "	105	105	104	102	99.5	98
<i>dl</i> - "	105	105	102.5	99	96.5	93
<i>d</i> -Camphorquinone	540	538	534	528	524	520
<i>l</i> - "	540	537	534	527	524	520
<i>dl</i> - "	540	537	528	520	514	508

DISCUSSION.

The magnitude of the polarisation depends on the electron charge density distribution and the effective radius of the molecule. The dipole moment determinations of the *d* and *l* forms show that the values of the stereoisomers agree closely with each other. This indicates that the electron charge distribution and radius in each of these stereoisomers would be identical and hence the total energy would be the same as postulated by the law of molecular dissymmetry.

The racemic forms bear the same dipole moment values as are possessed by the *d* and *l* forms, which shows that at the low concentrations at which the dipole moments are measured in order to eliminate the solvent effect, the racemic form behaves as if it were a mixture of *d* and *l* forms.

The total polarisation determinations of the *d*, *l* and *dl* forms show that at the same concentrations the values of the *d* and *l* forms agree closely, while those of *dl* forms always differ. The differences become more and more pronounced as the concentrations are increased. This fact shows that at low concentrations the racemic compound decomposes to give *d* and *l* forms. This is indicative of the presence of a weak bond in case there is a compound formation.

The authors acknowledge their thanks to Dr. B. K. Singh for supplying some of the compounds, and to Prof. Mahan Singh for facilities and assistance provided.

DEPARTMENTS OF CHEMISTRY AND PHYSICS,
GOVT. COLLEGE, LAHORE.

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REVIEWS

Volumetric Analysis. Vol. II. Titration Methods.—By I. M. Kolthoff and V. A. Stenger. 2nd revised edition, 1947. Published by Interscience Publishers Inc., New York. Royal 8vo. Pp. 374 + xiii.

The present volume deals with titration methods involving acid-base, precipitation and complex formation reactions. Oxidation-reduction methods have been reserved for a third volume, scheduled to be published late this year.

Prof. Kolthoff is well known by his series of brilliant text-books and monographs on quantitative analysis. The present book is in line with its predecessors in the rationalized approach to the evaluation of different methods with his characteristic precision and insight.

The book contains selected methods discussed critically and comprehensively. The chapters on acid-base reactions include, besides a thorough discussion on simple acidimetry and alkalimetry, displacement titrations, hydrolytic titrations such as the use of potassium palmitate, and special methods like the formation of mercuric complexes, bromo-acidimetry etc. The last three chapters contain a very complete account of argentometric and mercurimetric titrations. A useful table of 'rational' atomic weights of elements referring to weighings in air in place of '*in vacuo*' international values has been given in the Appendix, which should find general adoption in analytical laboratories to eliminate an error which, as the author has pointed out, may go up to 0.1% "consciously committed" in calculations.

The book is profusely foot-noted with select references and has both a subject index and an author index. The quality of paper and printing leave little to be desired.

J. G.

The Elements of Physical Chemistry.—By Samuel Glasstone. Published by D. Van Nostrand Company Inc., New York. Third printing, 1947. Pp. 695 + vi.

The difficulties of presenting the fundamentals of the whole of physical chemistry in an elementary book are easily realisable. But the author has done the job admirably well. Particular mention should be made of the nice presentation of the subject matters, and that without any vagueness and inexactitude, which are usual features in elementary books. In fact, several knotty points have been satisfactorily dealt with. A discussion on osmosis and osmotic pressure is enlightening in this respect.

The students will find the review questions and the problems very helpful and instructive.

The reviewer would like to mention a few omissions in the way of suggesting improvements: a simple deduction of the phase rule; thermodynamic basis of Trouton's rule; mention of chemical potential and fugacity in Chapter XI; a section on units of concentration and their mutual relationships; and a section on partial molar properties.

The implications of section 38c will not possibly be intelligible to the readers of this book.

S. K. M.

The Theory of Valency and the Structure of Chemical Compounds.—By Prof. P. Rây. Cooch-Bihar Professorship Lectures for 1941. Published by the Indian Association for the Cultivation of Science, Calcutta, 1946. Price Rs. 3/-

The burden of maintaining a close acquaintance with the forward movement of science must be felt by all keen minds engaged in any form of scientific activity. With the widening and deepening of knowledge, the independence of individual fields of research has become a thing of the past, and keeping abreast of science in general has ceased to be hobby of a few, but has become essential for everyone's own work. Progress reports are therefore in increasing demand, whether they appear as monographs, hand-books, annual reviews, or lectures. Where a personal interpretation by the reporter or lecturer stands in the foreground, a coherent and valuable picture results. Such is the case with the Cooch-Bihar Professorship lectures on "The theory of valency and the structure of chemical compounds" given by Professor P. Rây at the Indian Association for the Cultivation of Science, Calcutta.

This volume presents a most welcome and important contribution, though the scope of the book is limited by the exigencies of the lectures. The book is divided into six chapters. The opening one on the classical theories of valency has been tailored rather austere. It is followed by a chapter on partial and residual valency and the classification of chemical compounds on the basis of Werner's theory of valency. A general review of the electronic theory of valency is given in the next chapter. Then comes the most important chapter of the book on the electronic structure of atoms and molecules and the modern quantum theory of valency. One of the most important consequences of the application of quantum mechanics to problems of molecular structure has been the introduction of the idea of "resonance hybrids". The actual state of a molecule is regarded as corresponding to resonance between two or more structures which possess different electronic configurations. A similar viewpoint has also been adopted for the individual bonds in the molecule. The phenomenon of resonance has been fully dealt with in the fifth chapter. The final chapter gives rather too brief an account of valency in ionic crystals.

Professor Rây is to be congratulated upon having produced such an excellent book. The completeness of references will be particularly valuable. There is no doubt that the book will prove useful to advanced students as a ready source of information on all matters covered by its title, saving laborious search through scattered literature. The mathematical treatment, upon which the modern theories of valency and molecular structure rest, has been purposely neglected, but many helpful references are given for further reading. The volume will serve as an interesting and useful introduction to the subject. The addition of an index would have increased the utility of the book.

R. C. R.

Contribution to the Knowledge of the Influences of Gonadotropic and Sex Hormones on the Gonads of Rats (Monograph on the progress of research in Holland).— By J. H. Gaarenstroom and S. E. de Jongh. Published by Elsevier Publishing Company, Inc., 1946. Pp. 164. Price 16s net.

The second world war isolated the scientists of the Netherland from the rest of the world. Undaunted by this misfortune they carried on their investigations with a grit and determination that must inspire admiration in the fellow investigators all over the world. This monograph is an attempt to acquaint us with their important findings on the effect of Gonadotropic and Sex Hormones. A critical reader cannot but be impressed by the record of their achievements in the realm of endocrinology. With logical precision, they developed their idea regarding the role of sex and gonadotropic hormones. In this monograph, we find admirably co-ordinated scientific observations throwing new light on the functions of these hormones. Photomicrographical records of tissue changes and abstracts of researches on allied subjects have been judiciously appended in the book. Thus we get an admirable picture of certain aspects of endocrinological researches in the Netherland, which was so long inaccessible to us. Congratulations are also due to the editors of this monograph, who are thus attempting to forge this world into One World in spite of the devastating war tearing it asunder.

P. B. S.

STUDIES IN GLASS SYSTEM. MAGNETIC SUSCEPTIBILITY OF
ALKALI SULPHATES DISSOLVED IN BORAX-GLASS
AND IN AQUEOUS SOLUTION

BY SUBODH KUMAR MAJUMDAR AND SANTANU MAJUMDAR

In previous investigations, one of us (S.K.M.) has examined the change in diamagnetic susceptibility of salts dissolved in borax-glass by the Guoy balance and the more accurate torsion balance. It has been found that polar crystals such as alkali halides, sulphates, etc. show large increase of magnetic susceptibility in the dissolved state in the glass over their normal values. In the present paper, a comparison has been made between the diamagnetic susceptibilities of alkali sulphates in aqueous solution and in solution in borax-glass, the measurements being made by the torsion balance and in similar concentrations, as far as possible, subject to the restriction of solubility. The results in every case bear out the conclusion previously reached, that the diamagnetic susceptibility of the dissolved salt increases in solution in glass quite out of proportion with the small increases observed in aqueous solutions. The observed increase is difficult to explain, but a tentative explanation of the abnormal increase of the susceptibility is given.

Glass systems containing different polar salts in a state of solution have been studied in our laboratory in a series of investigations, in which mole-refraction, X-ray diffraction patterns and magnetic susceptibility of the dissolved salts have been examined. A rather remarkable result has been obtained from measurement of diamagnetic susceptibility of polar salts dissolved in boric oxide and borax-glasses (Majumdar and Saha, *J. Indian Chem. Soc.*, 1945, **22**, 147; Majumdar and Banerjee, *Indian J. Phys.*, 1946, **18**, 217; Majumdar, *Nature*, 1948, **161**, 658). It has been found that the diamagnetic susceptibility of a salt like NaCl or Na₂SO₄, dissolved in borax-glass, as calculated from the additivity rule from the experimental value, is very much greater than its normal value. In the case of salts containing different cations, the discrepancy may in part be attributed to cationic exchange. But the explanation has to be sought elsewhere in cases of glass systems, like NaCl—Na₂B₄O₇ or Na₂SO₄—Na₂B₄O₇. As some of the former experiments referred to were carried out with Guoy balance, the accuracy of which is not great, it was thought desirable to extend the investigation with a more accurate instrument, namely the Magnetic torsion balance described by Krishnan and Banerjee (*Phil. Trans.*, 1935, **A**, **234**, 265) and to measure side by side the change in susceptibility of these salts in aqueous solutions with the same instrument.

EXPERIMENTAL

Preparation of the Samples.—Borax was recrystallised from conductivity water twice and completely dehydrated first in air-oven at 250° and then in a vacuum desiccator, until a small quantity taken in absolute alcohol did not colour anhydrous copper sulphate. The salts (Merck) were likewise recrystallised once and dehydrated. Lithium sulphate was prepared as described in a previous communication (Majumdar and Banerjee,

loc. cit.) by dissolving lithium carbonate in pure H_2SO_4 and twice recrystallising in a vacuum desiccator.*

Determination of Magnetic Susceptibility.—The magnetic susceptibility of the glass samples, as also of the pure constituents, was determined in a magnetic torsion balance (Krishnan and Banerjee, *loc. cit.*) and modified later by Dutta (*Indian J. Phys.*, 1944, **18**, 249). The glass pieces were attached to one end of a stout pyrex glass rod of suitable length, the other end being attached to the middle of a fine silver wire stretched horizontally between a graduated torsion head and a metal chuck. For solutions, a fine quartz wire was used instead of the silver wire. This increased the sensitivity of the instrument. For experiments with aqueous solutions, a piece of iron pyrite was attached to the end of the glass rod. The crystal of pyrite or the glass, as the case may be, was kept at a distance of 2 to 3 cm. away from the vertical sides of the flat pole pieces of a powerful electromagnet (about 2000 gauss), the gradient of the field being in the horizontal direction. The solid was attached in such a way that its basal plane was parallel to the direction of the uniform part of the field. In this way only the horizontal gradient of the field was effective in laterally displacing the solid, the wire being sufficiently stretched. The whole apparatus was enclosed in a case to protect it from dust and wind.

The glass was suspended in a liquid of known susceptibility and was viewed through a tele-microscope, so that one of the edges coincided with the scale marks. On switching the current, the solid moved laterally along the gradient in a direction away from the field, as all systems studied were diamagnetic. The torsion head was then slowly turned until the edge of the glass returned to its original position. The current was kept constant through regulating rheostats. The liquid was then replaced by another liquid, also of known susceptibility and the procedure repeated.

If κ_0 be the volume susceptibility of the glass and κ_1 and κ_2 , that of the two liquids; A , the cross section of the glass piece; H_x , the field strength, the horizontal direction being the x -direction, and θ_1 and θ_2 , respectively the angles through which the torsion head is turned in the two liquids and R , the torsional constant of the wire,

$$\text{then} \quad \frac{1}{2} A H_x \cdot \frac{dH_x}{dx} (\kappa_0 - \kappa_1) = R \cdot \theta_1 \quad \dots \quad (1)$$

$$\text{and} \quad \frac{1}{2} A H_x \cdot \frac{dH_x}{dx} (\kappa_0 - \kappa_2) = R \cdot \theta_2 \quad \dots \quad (2)$$

Dividing (1) by (2)

$$\frac{\kappa_0 - \kappa_1}{\kappa_0 - \kappa_2} = \frac{\theta_1}{\theta_2} \quad \dots \quad (3)$$

As all the quantities excepting κ_0 are known, the latter may be calculated from the equation. The mass susceptibility (χ) was found out by dividing κ_0 by the density of the

* The authors are indebted to Prof. P. B. Sarkar of the University College of Science, Calcutta for the sample.

sample determined in a hydrostatic balance. The liquids selected were Schering-Kahlbaum's pure pyridine ($\chi = -0.623 \times 10^{-6}$) and Merck's pure diethylaniline ($\chi = -0.835 \times 10^{-6}$), both freshly redistilled. It is clear that wider the difference in the values of χ of the two liquids, the larger will be the values of θ , and hence greater the sensitivity of the measurements. For aqueous solutions, conductivity water ($\chi = -0.720 \times 10^{-6}$) was first used with iron pyrite and then with the solutions.

The density of the solid pieces was determined by a hydrostatic balance, using nitrobenzene as the immersion liquid. The suspension was made with a single fibre of unspun silk to minimise the capillary rise of the liquid. The density of nitrobenzene, as also of the different aqueous solutions, was made in a specific gravity bottle in air simultaneously with the magnetic measurements.

Analysis of the Samples.—The samples of glass were analysed by taking a definite weight, dissolving it in hot water and acidifying with pure HCl. The sulphate was precipitated by BaCl₂ in the usual way and the precipitated BaSO₄ weighed. The samples of precipitated BaSO₄ after washing and weighing did not respond to the test of borate by burning it with a mixture of alcohol and H₂SO₄, indicating that no barium borate was precipitated.

The following tables show the data for magnetic susceptibility measurements for aqueous solutions.

TABLE I

Volume susceptibility (κ) of aq. solns. of Li₂SO₄, Na₂SO₄ & K₂SO₄ at diff. conc.

$\kappa_0 = -0.789 \times 10^{-6}$ (Fe-pyrite). $\kappa_1 = -0.720 \times 10^{-6}$ (water).

No. of sample.	% of salt.	θ_1 (mean) in condy. water. Li ₂ SO ₄ solution.	θ_2 (mean) in soln.	κ_2 (vol. sus. of soln.) $\times 10^{-6}$.
1	6.23	365°.8	366°.7	-0.7236
2	9.31	385°.0	389°.4	-0.7371
3	12.10	372°.7	379°.7	-0.7482
4	16.04	375°.2	386°.3	-0.7648
Na ₂ SO ₄ solution.				
1	4.73	386°.0	388°.7	-0.7304
2	7.123	378°.0	382°.0	-0.7359
3	10.156	356°.0	362°.2	-0.7461
4	14.302	363°.0	372°.4	-0.7591
5	17.987	385°.0	398°.0	-0.7710
K ₂ SO ₄ solution.				
1	2.50	378°.0	379°.5	-0.7257
2	5.14	372°.5	375°.4	-0.7319
3	7.62	384°.0	388°.7	-0.7385
4	10.04	379°.5	385°.9	-0.7453

TABLE II

Determination of density.

Li_2SO_4 solution ($t=27.6^\circ$).		Na_2SO_4 solution ($t=26.0^\circ$).		K_2SO_4 solution ($t=26.3^\circ$)	
% of salt.	Density of soln.	% of salt.	Density of soln.	% of salt.	Density of soln.
6.23	1.032	4.73	1.039	2.5	1.018
9.31	1.064	7.123	1.059	5.14	1.038
12.90	1.093	10.156	1.090	7.62	1.059
16.04	1.128	14.302	1.130	10.04	1.079
		17.987	1.166		

TABLE III

Observed values of χ of aq. soln. of salts and their deviation from the calc. values.

% Composition of salt.	$\kappa_s \times 10^6$ of soln.	Density of soln.	$\chi \times 10^6$ of solution		Diff. (obs. - calc.) $\times 10^6$.
			Obs.	Calc.	
Li_2SO_4 solution (water).					
6.23	-0.7236	1.032	-0.70115	-0.6988	-0.00235
9.31	-0.7371	1.064	-0.69279	-0.6883	-0.00449
12.90	-0.74824	1.0937	-0.68413	-0.67613	-0.00800
16.04	-0.7648	1.1283	-0.67783	-0.66546	-0.01237
Na_2SO_4 solution (water).					
4.73	-0.73042	1.0392	-0.70287	-0.70189	-0.00098
7.123	-0.73594	1.0595	-0.69459	-0.69270	-0.00189
10.156	-0.74614	1.0901	-0.68446	-0.68111	-0.00335
14.302	-0.75914	1.1307	-0.67137	-0.66520	-0.00617
17.987	-0.7710	1.1666	-0.66090	-0.65112	-0.00978
K_2SO_4 solution (water).					
2.50	-0.72577	1.0188	-0.71239	-0.7120	-0.00039
5.14	-0.73194	1.0389	-0.70451	-0.7037	-0.00081
7.62	-0.73857	1.0592	-0.69728	-0.69584	-0.00144
10.04	-0.74536	1.0795	-0.69047	-0.6882	-0.00227
χ for pure					
		Li_2SO_4	$= -0.38 \times 10^{-6}$		
		Na_2SO_4	$= -0.337$		
		K_2SO_4	$= -0.403$		
		water	$= -0.720$		

In the following tables the values of g : molecular susceptibilities (χ_m) of the three alkali halides are calculated from the additivity rule on the assumption that the value for water remains constant in solution, and the values are compared with similar values for glass systems, determined by the same method (Majumdar and Benerjee, *loc. cit.*).

TABLE IV

 Li_2SO_4 system.

Normal value of salt $\times 10^6 = -41.7$.

% Salt	Obs. χ of mixture $\times 10^6$	* χ of salt in soln. $\times 10^6$	χ_m of salt in soln. $\times 10^6$	% Salt	Obs. χ of mixture $\times 10^6$	* χ of salt in soln. $\times 10^6$	χ_m of salt in soln. $\times 10^6$
Li_2SO_4 aqueous solution.				Li_2SO_4 - $\text{Na}_2\text{B}_4\text{O}_7$ -glass.			
6.23	-0.70115	-0.41765	-45.91	7.02	-0.5846	-1.1543	-126.89
9.31	-0.69279	-0.42788	-47.04	9.55	-0.6759	-1.9479	-214.15
12.90	-0.68413	-0.44190	-48.58	11.50	-0.7145	-2.0452	-224.81
16.04	-0.67783	-0.45718	-50.26	12.98	-0.7643	-2.2574	-248.18

*from additivity rule.

TABLE V

 Na_2SO_4 system.

Normal value of salt $\times 10^6 = -47.87$.

% Salt	Obs. χ of mixture $\times 10^6$	* χ of salt in soln. $\times 10^6$	χ_m of salt in soln. $\times 10^6$	% Salt	Obs. χ of mixture $\times 10^6$	* χ of salt in soln. $\times 10^6$	χ_m of salt in soln. $\times 10^6$
Na_2SO_4 aqueous soln.				Na_2SO_4 - $\text{Na}_2\text{B}_4\text{O}_7$ -glass			
4.73	-0.70287	-0.35776	-50.82	8.68	-0.6195	-1.4389	-204.40
7.123	-0.69459	-0.36313	-51.58	10.67	-0.6591	-1.6428	-233.37
10.156	-0.688446	-0.37004	-52.56	13.43	-0.7292	-1.9384	-275.35
14.30	-0.67137	-0.3800	-53.98	15.62	-0.7752	-2.0372	-289.38
17.98	-0.66090	-0.39130	-55.59	17.36	-0.8455	-2.2922	-325.60
				17.71	-0.8563	-2.3186	-329.35

TABLE VI

 K_2SO_4 system.

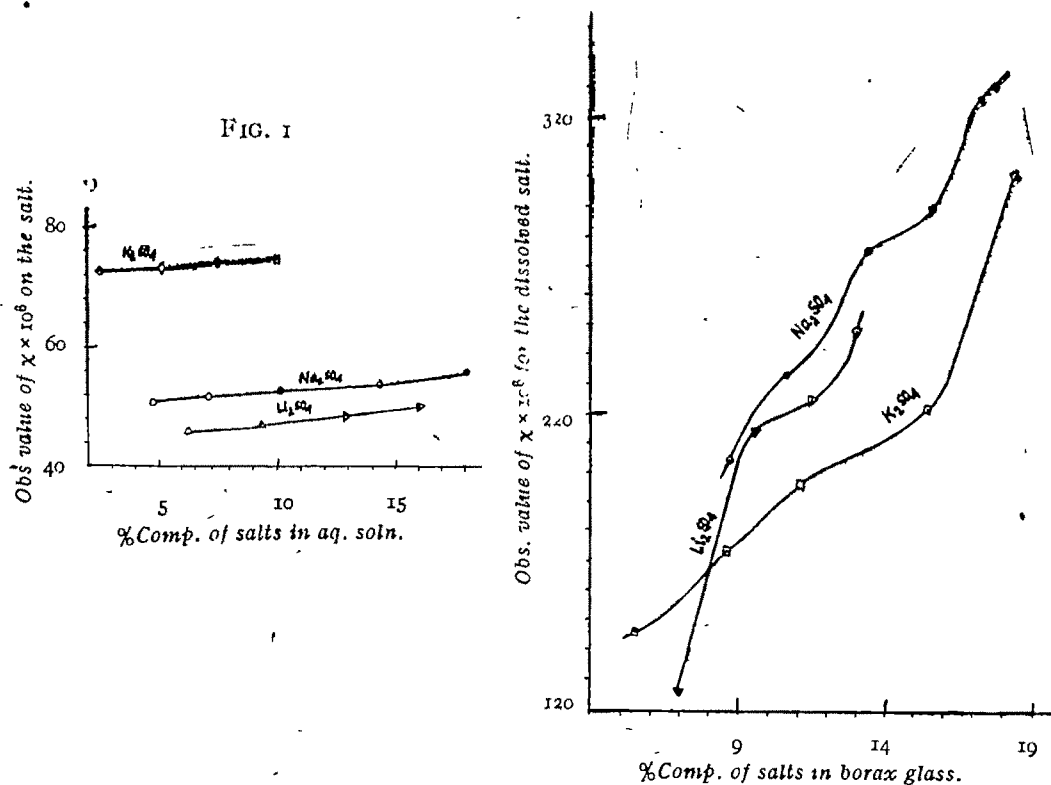
Normal value of salt $\times 10^6 = -70.22$.

% Salt	Obs. χ of mixture $\times 10^6$	* χ of salt in soln. $\times 10^6$	χ_m of salt in soln. $\times 10^6$	% Salt	Obs. χ of mixture $\times 10^6$	* χ of salt in soln. $\times 10^6$	χ_m of salt in soln. $\times 10^6$
K_2SO_4 -aqueous soln.				K_2SO_4 - $\text{Na}_2\text{B}_4\text{O}_7$ -glass.			
2.50	-0.71239	-0.41640	-72.557	5.46	-0.5580	-0.84176	-146.68
5.14	-0.70451	-0.41886	-72.986	8.64	-0.5810	-0.99759	-173.83
7.62	-0.69729	-0.42198	-73.530	11.14	-0.6070	-1.1286	-196.67
10.04	-0.69047	-0.42581	-74.196	15.38	-0.6540	-1.2724	-221.72
				18.42	-0.7580	-1.7165	-299.10

*from additivity rule.

In order to ensure that the abnormally high values of susceptibility in the case of alkali sulphates dissolved in borax-glass were not due to experimental error (these values being taken from Majumdar and Banerjee, *loc. cit.*), fresh experiments were carried out

FIG. 2



with the Na_2SO_4 — $\text{Na}_2\text{B}_4\text{O}_7$ —glass system, in which the possibility of cationic exchange was excluded. It will be seen from the curve that it is not materially different from the corresponding one in the previous set of experiments.

TABLE VII

Na_2SO_4 — $\text{Na}_2\text{B}_4\text{O}_7$ —glass system.

Wt. of sample.	Analysis of the glass.		
	Wt. of BaSO_4 .	Wt. of Na_2SO_4 (calc.)	% of Na_2SO_4 .
0.9336 g.	0.1718 g.	0.1046 g.	11.20
0.9977	0.2390	0.1455	14.58
0.8669	0.2820	0.1717	19.80

TABLE VII (contd.)

 $\text{Na}_2\text{SO}_4\text{--Na}_2\text{B}_4\text{O}_7\text{--glass system.}$

Magnetic susceptibility data.					
% Na_2SO_4 .	θ_1 (mean) in pyridine.	θ_2 (mean) in diethylaniline.	$^*\kappa_s \times 10^6$ (from A. R.)	Density of sample.	χ of glass $\times 10^6$.
11.20	175°.0	147°.8	-1.693	2.547	-0.6647
14.58	195°.5	172°.0	-2.011	2.723	-0.7385
19.80	220°.0	199°.0	-2.375	2.656	-0.8947
0 (pure borax glass)	115°.0	86°.0	-1.279	2.357	-0.5427

Calculated χ_M of Na_2SO_4 in glass.

% Na_2SO_4	Obs χ of glass $\times 10^6$.	χ of Na_2SO_4 in glass (calc.) $\times 10^6$	χ_M of Na_2SO_4 in glass (calc.) $\times 10^6$.	χ_M of pure $\text{Na}_2\text{SO}_4 \times 10^6$.
11.20	-0.6647	-1.632	-231.9	
14.58	-0.7385	-1.886	-268.0	-47.87
19.80	-0.8947	-2.320	-329.7	

* "A. R." denotes analytical results

DISCUSSION

If χ be the observed mass susceptibility of the glass or aqueous solution and χ_1 and χ_2 , the values for pure borax glass or water and the salt in glass or in solution respectively, then according to the additivity rule,

$$100\chi = p \cdot \chi_1 + (100 - p) \cdot \chi_2.$$

Assuming the susceptibilities of borax glass and water to remain unaltered (-0.5417×10^{-6} and -0.720×10^{-6} respectively), the values for the salt in glass or in aqueous solution may be calculated. These values are shown in Tables IV-VII.

It will be seen that while in aqueous solutions the values of χ for the dissolved salts increase but little with concentration, the discrepancy between the calculated and normal values in glass solutions are far too large to be explained away by experimental error.

According to the simple theory of diamagnetism, χ is given by

$$\chi = -\frac{N \cdot e^2}{6 m c^2} \sum_n r^2,$$

where the symbols have their usual significance. Putting the numerical values of the constants, the equation reduces to

$$\chi = -2.832 \sum r^2 \times 10^{10}.$$

As $\sum r^2$ represents the sum of the projected electronic orbits, increase in the values of χ will mean an increase in the values of $\sum r^2$, which in the case under examination would point to an increased spacing in the crystal.

The results of X-ray diffraction experiments on these systems (Majumdar and Banerjee, *loc. cit.*) reveal the existence of crystallites in the glass, but the spacings, as measured by these methods, do not seem to have undergone any appreciable change. Refraction measurements indicate on the other hand an abnormally low value of mole-refraction for the dissolved salt (Majumdar and Banerjee, *J. Indian Chem. Soc.*, 1946, **23**, 171). An abnormally small value of the latter is indicative of a very large deformation of the crystals in the glass and this fact can also not be interpreted in the light of magnetic measurements, which distinctly point to an enlargement of the lattice. The explanation of this anomaly is therefore of very great theoretical interest. That the lattice dimension of a crystal can undergo change without altering the crystal form has been hinted on theoretical grounds among others by Lennard Jones (*Z. Krist.*, 1930, **76**, 215) and others, who have calculated the extent of mutual polarising influence of different molecules (?) of the crystal on one another. But in no case is the increase more than a few per cent of the normal values. The size of the crystallite particles of the salts dispersed in the glass therefore may have something to do with the observed abnormally large values, but it cannot clearly explain the increase.

With regard to the aqueous solutions, the observed increase is in keeping with the results obtained by different workers like Veiel (*Ann. Physik*, 1935, **24**, 697), Flordal and Frivold (*ibid.*, 1935, **23**, 425), Frivold and Sogn (*ibid.*, 1935, **23**, 413) and others, who have all found a decrease in the experimental value of the susceptibility of the solutions, from their calculated values from the additivity rule which means an increase in the values of the dissolved salts over their normal values. Frivold and Sogn (*loc. cit.*) have found that the calculated values of χ of various salts in aqueous solution are greater than in alcoholic solutions. This is quite understandable if one takes into account the effects of ionisation and hydration in aqueous medium.

On the other hand, a few workers like Varadachari (*Curr. Sci.*, 1934, **3**, 249) have found no change from additivity rule in aqueous solutions of different salts including sodium sulphate and the values found are not materially different from those of the pure crystals, which is rather difficult to reconcile on theoretical grounds.

Several workers have found that the degree of subdivision of the dispersed phase in a dispersed medium affects the magnetic properties of the former. Thus, Bhatnagar (*J. Indian Chem. Soc.*, 1930, **7**, 357), Rao (*Indian J. Phys.*, 1931, **6**, 241) and others have found that in colloidal solutions of antimony and bismuth, the diamagnetism of the metals is actually less than in the metals in the massive condition. Goetz (*Phys. Rev.*, 1932, **39**, 169) from a study of graphite particles has found that above a certain size diamagnetism is independent of particle size and it decreases below a critical size (1.5×10^{-6} cm.). Prin (*Nature*, 1935, **136**, 299) has also found a smaller value of diamagnetism for colloidal solutions of metals. Thomson (*Proc. Roy. Soc.*, 1931, **A**, 115,

133) on the other hand has found from electron diffraction experiments that electrolytically deposited copper has a larger spacing than ordinary copper.

In all the cases examined by us, as also in the case of noble metals like gold and platinum dispersed in borax glass (the results of which form the subject matter of separate communications) there is an abnormal increase of diamagnetism in a glass solution. Majumdar and Palit put forward an explanation concerning the role of the dielectric medium on the Coulomb and the short distance forces operating within a polar crystal lattice (*J. Indian Chem. Soc.*, 1942, 19, 461). According to this view, the equilibrium of a strictly polar lattice is brought about by the action of mainly two forces, the electrostatic forces between the charged ions, which follow the Coulomb law, and a short distance repulsive force, which decreases much more rapidly with the distance than the former (inversely as the seventh or the ninth power of the distance) (cf. Born and Lande, *Verhand. deuts. physikal. Ges.*, 1918, 20, 210). The potential of a single ion in the lattice (u) in a vacuum may be expressed by means of the equation,

$$u = \frac{A.e^2}{d} + \frac{B}{d^n},$$

where A and B are constants called Madelung constants and d is the distance of the ion from a central ion. With the interposition of a medium of dielectric constant D , the potential will be altered to u' such that

$$u' = \frac{A.e^2}{D.d'} + \frac{B}{D.d'^n}, \text{ where } d' > d.$$

The dielectric constant of borax glass is 7.5 (Landolt-Börnstein Tables). And hence it may be inferred that with the weakening of the electrostatic and other forces, the lattice dimensions will be increased.

There are, however, serious objections to this view. In water, which has a very high dielectric constant, the lattice is completely destroyed and the ordered arrangement obtaining in the crystal is absent in aqueous solutions as seen from the weak haloes which the latter give in X-ray diffraction experiments. But inspite of this, the departure from the additivity rule, so far as diamagnetism is concerned, is not very marked and can be explained by hydration and other effects of the ions. Why should therefore be such an abnormal increase in diamagnetism of the same salts when dispersed in a glass? This is a question which requires clarification.

The increase in diamagnetism according to some may be due to what is called Raman-Ehrenfest binding of the valency electrons, in which these are supposed to have large orbits encircling a relatively large number of atoms or ions, but the abnormal increase observed by us cannot be explained by such an assumption.

Whether a continuous lattice of the dispersed salt is formed in the glass medium also requires elucidation. According to recent theories about structure of glass due to Warren, Zachariasen and others, in glasses like borax, the periodicity obtaining in a true crystal is absent, and each boron atom is linked to three other boron atoms through three oxygen atoms forming a triangular configuration. It is also assumed that the cations like Na^+ or K^+ are joined by electrovalent linkage and take their positions

within the *hollows* of this non-periodic meshwork. It may be assumed in accordance with the theory postulated above, that when a new equilibrium results by the solidification of the melt, the Na^+ and SO_4^{2-} ions take up their positions within these hollows, conditioned by the altered electrostatic and other forces operating within the system. This, however, is also dependent on the dimensions of the hollows and on the lattice energies of the salts and of the glass meshwork.

It may be argued that the additivity rule does not hold good in such a system. This is tantamount to saying that the values of susceptibilities of the constituents in the additivity equation would not correspond to their normal values, if the value for the observed susceptibility of the glass is to fit in the equation. It is probable therefore that in such a case, the susceptibility of borax, which we have taken to be constant, actually undergoes some variation in the glass.

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CHEMICAL LABORATORIES,
PRESIDENCY COLLEGE, CALCUTTA.

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STUDIES IN GLASS SYSTEM. MAGNETIC SUSCEPTIBILITY OF GOLD DISPERSED IN BORAX-GLASS

BY SUBODH KUMAR MAJUMDAR AND GURU PRASAD BASU-CHAUDHURY

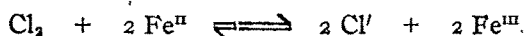
The diamagnetic susceptibility of gold, dispersed in borax glass, has been measured at different concentrations by the magnetic torsion balance. It has been found that the susceptibility of dissolved gold, as calculated from the additivity formula, is greater than the value for pure gold, although the increase is not so high as in the case of alkali sulphates and chlorides, dispersed in the same glass. The reason for this increase has been discussed.

Several papers on the properties of polar crystals and noble metals, dissolved in boric oxide and borax glasses, have been published by Majumdar and co-workers. The magnetic properties of such systems have been recorded in three communications (Majumdar and Saha, *J. Indian Chem. Soc.*, 1945, **22**, 147; Majumdar and Banerjee, *Indian J. Phys.*, 1946, **18**, 217; Majumdar and Majumdar, *this issue* p. 291; Majumdar, *Nature*, 1948, **161**, 685). In these investigations it has been found that alkali chlorides and sulphates show an abnormal increase of diamagnetic susceptibility when dispersed in boric oxide or borax glasses and the increase is quite out of proportion with the value observed in the case of aqueous solutions of these salts. With systems having a salt containing a different cation in borax glass, the observed change may in part be accounted for by cation exchange in the glass. But, noble metals like gold and platinum are not known to form any borates and, hence any change observed in such a system is not due to any compound formation. It is for this reason that gold was selected as the dispersed phase and the magnetic susceptibility of the glass samples was determined. Similar systems with platinum (paramagnetic) have also been studied and will form the subject of a separate communication.

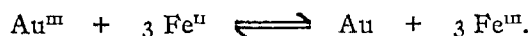
EXPERIMENTAL

Preparation of the samples.—Purified samples of borax (Merck, pro-Analyse quality) were prepared as described in a previous communication (Majumdar and Majumdar, *loc. cit.*). The precaution is necessary as traces of moisture are tenaciously held by glass—even if it melted at such a high temperature as 1000° (Turner). An 1% solution of pure gold chloride was prepared in conductivity water and a definite volume was taken in a clean platinum crucible and the solution evaporated on a water-bath. The crucible was then heated on asbestos to about 300° to ensure complete decomposition of gold in a finely divided state. A roughly weighed amount of purified and dehydrated borax was then added and the mixture heated to 800°—1000° until a homogeneous melt was obtained. Above a certain concentration of gold, the excess of the metal separated on the surface and did not enter into the system. The maximum gold content, as found by subsequent analysis, was 3.12%. The crucible was allowed to cool gradually and the solid extracted. The glass was lightly coloured, the shade varying from light grey to pink in transmitted light.

Analysis of the samples.—The percentage of gold in the samples was determined by an electrometric method due to Müller and Weisbrod (*Z. anorg. Chem.*, 1926, 17, 156). To test the accuracy of the method for small concentrations of gold, a standard solution was prepared by dissolving 0.5 g. of pure gold in aqua regia, evaporating the solution on a water-bath and diluting it to 200 c.c. A sudden fall of potential was observed when all the excess of chlorine water was used up:



and the solution contained only trivalent gold. The titration was continued when another sudden drop in potential was observed due to the reduction of trivalent gold to metallic gold:



The amount of FeSO_4 consumed between these two breaks gave the equivalent of Mohr salt corresponding to the gold present. The precipitated gold was sometimes deposited on the electrode, but the results were reproducible in spite of it. Addition of borax lowered the first potential drop by 50 millivolts or so, but the break was quite sharp. The shape of the curve near the first equivalence point was slightly changed. Unfortunately these were not perfectly reproducible. As the equivalence point was calculated from the $(\Delta E/\Delta V, c)$ curves, the actual shape of the curves did not have much effect on the equivalence points found and did not therefore much affect the results.

Determination of the Magnetic Susceptibility of the samples.—The diamagnetic susceptibility of the samples was determined in a magnetic torsion balance as described in a previous communication (Majumdar and Majumdar, *loc. cit.*). The density of the glass sample was then determined by noting the loss in weight in a hydrostatic balance, suspended in a liquid of known specific gravity (nitrobenzene, sp. gr. = 1.1999).

FIG. 1

Gold titration curve with FeSO_4 (no borax).

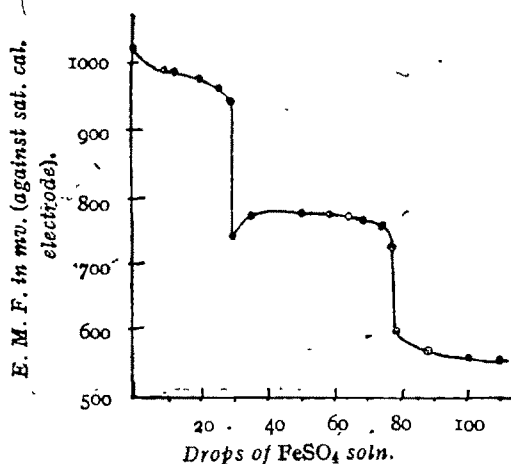
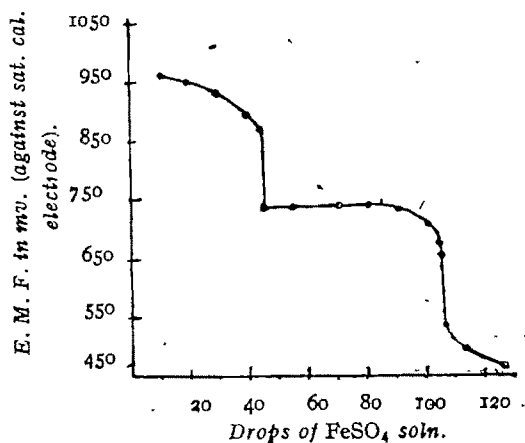


FIG. 2

Gold titration curve with FeSO_4 (in presence of 200 times borax).



A standard solution of gold was prepared by dissolving 0.5152 g. of purest sample of gold available in aqua regia, evaporating the solution on a water-bath and making the solution up to 250 c.c. A more dilute solution was prepared by diluting 25 c.c. of this solution to 250 c.c. (1 c.c. \equiv 0.0002576 g. of gold). The Mohr salt solution contained 0.01102 g. equiv. per litre. Thus 1 c.c. of the soln. \equiv 0.0007243 g. of Au.

The potentials were measured in a Tinsley potentiometer (Vernier type) against a saturated calomel electrode at room temperature and represented graphically in Figs. 1 and 2.

The following table gives the results of titration with standard gold solutions with and without borax (curves 1, 2, 3).

TABLE I

Titration with standard gold solution.

Au taken (mg.)	... 2.576 (without borax)	0.6645 (without borax)	0.8316 (with borax)
„ found „	... 2.568 (Fig. 1)	0.6539 (Fig. 2)	0.8302 (Fig. 3)

The following table gives the results of gold estimation with different samples of borax glass.

TABLE II

Amount of glass dissolved in 50 c.c. (g.)	... 0.4162	0.3898	0.2769	0.2859	0.2287	0.3004	0.4769
% Au in the sample	... 0.294	1.04	1.284	1.53	1.873	2.23	3.01

Table III gives the values of susceptibility determination of the different samples; density of the different samples of borax glass in nitrobenzene (found, in air at 35°, 1.1999) is shown in column 5. The variation in the specific gravity of glass of the same composition, as is well known, is due to different rates of annealing. This has no effect on the value of the mass susceptibility as will be seen in the following table.

TABLE III

Immersion liquids employed: pyridine ($\kappa_1 = -0.612 \times 10^{-6}$) and diethylaniline ($\kappa_2 = -0.780 \times 10^{-6}$). Density of nitrobenzene found (temp. of air = 35°) = 1.1999.

% Au	θ_1	θ_2	Vol. sus. κ_0 from	Sp. gr.	$\chi \times 10^6$
			$\frac{\theta_1}{\theta_2} = \frac{\kappa_0 - \kappa_1}{\kappa_0 - \kappa_2} \times 10^6$		
0 (Sample I)	83°.3	63°.3	-1.264	2.334	-0.5418
0 („ II)	100°.0	75°.0	-1.284	2.371	-0.5414
0 („ III)	87°.8	65°.4	-1.2706	2.346	-0.5416
0.294	130°.1	100°.4	-1.348	2.4939	-0.5404
1.040	78°.3	55°.5	-1.189	2.2122	-0.5375
1.284	84°.5	60°.6	-1.206	2.2478	-0.5365
1.530	106°.6	80°.4	-1.295	2.4180	-0.5356
1.873	116°.9	85°.9	-1.246	2.3322	-0.5342
2.230	112°.45	85°.8	-1.321	2.4793	-0.5329
3.010	58°.1	43°.1	-1.2625	2.3823	-0.5298

It will be seen from the above table that there is a gradual decrease of the mass susceptibility of the glass with increasing concentration of gold. This observation is in keeping with the results of similar systems in which polar salts are dispersed, with the difference that the decrease is less in the case under examination.

DISCUSSION

From the observed values of χ for the glass, the mass susceptibility of dissolved gold χ_1 may be calculated from the additivity formula :

$$100\chi = p.\chi_1 + (100 - p).\chi_2,$$

where χ is the observed mass susceptibility of the glass, χ_1 , that of the dissolved gold, p , its percentage in the glass and χ_2 is the susceptibility of borax glass, which is taken as -0.5417×10^{-6} .

The following table shows the values of χ_1 and atomic susceptibility χ_A of the dissolved gold dispersed in borax glass.

TABLE IV

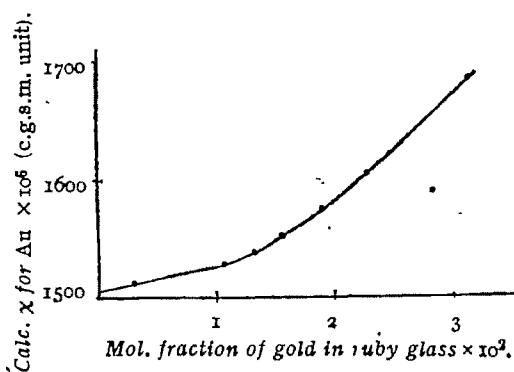
Conc. of Au.	$\chi_1 \times 10^6$ (calc.).	$\chi_A \times 10^6$ (calc.).	Conc. of Au.	$\chi_1 \times 10^6$ (calc.).	$\chi_A \times 10^6$ (calc.).
0.303%	-0.1512	-29.82	1.912%	-0.1574	-31.03
1.059	-0.1528	-30.13	2.280	-0.1604	-31.63
1.306	-0.1538	-30.33	3.150	-0.1682	-33.16
1.561	-0.1552	-30.61			

χ for pure Au = -0.1500×10^{-6} and $\chi_A = -29.58 \times 10^{-6}$.

The results are represented graphically in Fig. 3.

FIG. 3

Change in susceptibility of Au dissolved in borax.



Although in the case under examination, the increase of diamagnetic susceptibility is not so great as in the case of such systems as $\text{Na}_2\text{SO}_4 - \text{Na}_2\text{B}_4\text{O}_7$ glass, yet the observed increase (about 12 % for a gold content of 3.1%) is real and cannot be accounted for by

experimental error. The X-ray diffraction results do not reveal any marked change in the spacing of dissolved gold (Majumdar and Banerjee, *Nature*, 1946, 158, 753).

The glass samples examined by us gave sharp diffraction lines in Debye-Scherrer photographs as opposed from diffuse bands obtained with Zsigmondy's gold sols, proving that the process of subdivision of gold in the glass does not proceed to the same fine states as in the colloidal solution (10^{-7} cm). In some cases, slight increase in diamagnetism has also been noticed with subdivision. Thus Rao (*Proc. Ind. Acad. Sci.*, 1935, 2A, 249) has found somewhat larger diamagnetism for colloidal copper than in massive metal. In any case, the relation of magnetic properties of elements with their state of subdivision has not been clearly elucidated.

It should be stated here that the free electrons in the metallic bond might contribute to increased diamagnetism. The so-called Raman-Ehrenfest binding may be present in the glass solution: in this type of binding it is assumed that the valency electrons have large orbits encircling a relatively large number of atoms. Hence, the observed increase in the diamagnetism of gold, dispersed in borax glass, may be due to the expansion of the orbits of the electrons of the metallic bond. But it is doubtful whether the total increase can be explained in this manner.

Whether presence of a dielectric medium can alter the dimensions of a metallic lattice also requires considerations. Unfortunately, the energetics of metallic lattice has not been studied in the same manner as in the case of purely polar lattices. But it may be inferred qualitatively (in analogy to the case of a polar lattice) that a dielectric medium will tend to decrease the binding forces between the constituents of the lattice. As the dielectric constant of borax glass is about 7.5, it may be expected that the gold lattice will be somewhat enlarged when it is formed by the solidification of a melt of borax.

The slope of the curve ($\chi - c$) also presents some difficulties. The extrapolated value of χ for 100% Au does not evidently give the value for pure metal. It is not safe, however, to extrapolate a curve with a maximum concentration of a little over 3% for 100%. The nature of the curve might vary (although this is a purely theoretical possibility, as higher concentrations are not obtained without separation of gold) at higher concentrations of the metal, passing through a maximum point. The whole subject therefore requires clarification and further experiments on similar systems are in progress.

The authors' thanks are due to the authorities of the Indian Association for the Cultivation of Science, Calcutta, for permission to use the Torsion Balance. Thanks are also due to Mr. A. K. Dutt for help in the experimental determinations.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA,

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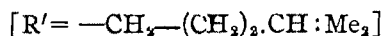
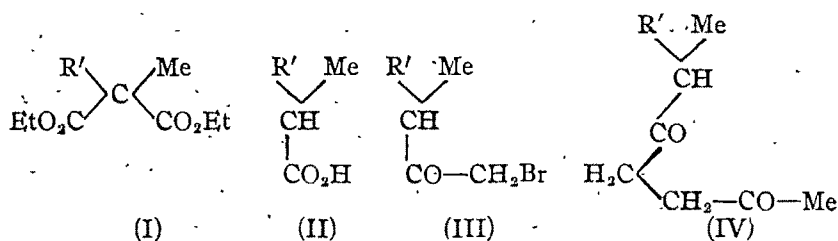
SYNTHESIS OF ALICYCLIC SYSTEMS RELATED TO STEROIDS. PART 1.

BY MOHAN CHAND MITTER AND PHANINDRA CHANDRA DUTTA

As a preliminary to the synthesis of 12-keto-steroids, attempts towards the synthesis of a tricyclic compound containing B, C and D rings have been described

Investigations described in the following pages deal with the exploratory work of somewhat varied nature with a view to finding out a general method for the synthesis of this type of alicyclic compounds incorporating the more salient features of the molecule. These pilot experiments are, however, limited to the building up of the fused system comprising B, C and D rings with the "C₁₃-methyl" group and the *iso*-octyl side-chain from simple *cyclohexane* and *cyclopentane* derivatives.

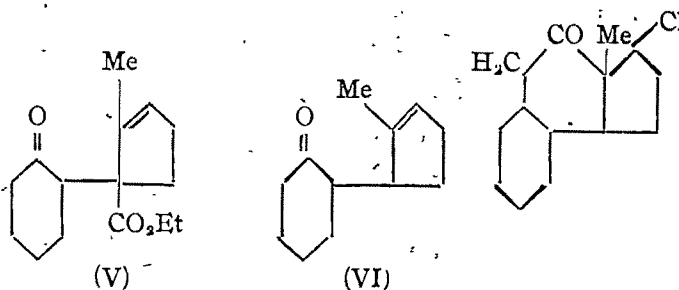
The main scheme of the work that has been originally chalked out may be depicted in the following manner :—



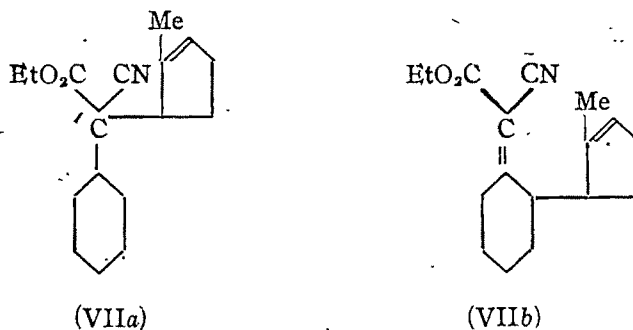
isoHexyl iodide condenses smoothly with ethyl methylmalonate to give (I), which on hydrolysis and decarboxylation leads to the formation of (II) in a very good yield. The acid chloride of this reacts with diazomethane in ethereal solution and from the diazo ketone, the bromoketone (III) is obtained on treatment with hydrobromic acid solution. This condenses smoothly with ethyl acetoacetate and the crude condensation product is hydrolysed with dilute alkali under the usual conditions with the expectation of obtaining the corresponding cyclopentene derivative (Ber., 1939, 72, 1590; 1942, 75, 448), but the product actually isolated corresponds to the diketone (IV). The attempts so far made for the closing up of the ring have met with failure. Action of alkali of different concentrations or use of dry sodium ethoxide effects no improvement in the process. A similar failure has also been met with in the use of sulphuric acid of varying concentrations or anhydrous oxalic acid. It is rather curious to note that the closing up of the cyclopentene ring from 1 : 4-diketones is almost instantaneous, but in this case no useful product could be isolated.

Next, the following line of attack has been pursued which can be graphically represented below.

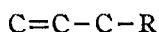
A preliminary note appeared in the *Science & Culture*, 1943-44, 9, 505.



Here the *iso*-octyl residue has been dropped leaving therein the possibility of introducing it at a later stage. Methylcyclopentene has been oxidised in acetic anhydride solution with selenium dioxide (Dane, *Annalen*, 1937, 532, 35) but the isolation of the acetate of 2-methyl- Δ^2 -cyclopentenol presents unusual difficulties. Consequently, the original process has been modified to the extent of extracting the acetate with ether and removing all acidic impurities by washing with a saturated solution of sodium carbonate. The acetate has been hydrolysed under the usual conditions and the ketonic impurity is removed by washing with a saturated solution of sodium bisulphite. The alcohol is obtained in a very poor yield, barely reaching 5% of the theory. It is, however, converted into the bromide which condenses smoothly with the potassium salt of cyclohexanone carboxylic ester to give (V). The ester is hydrolysed with baryta and the ketone (VI) is isolated in a very poor yield along with a considerable amount of the high boiling product. To avoid the process of alkaline hydrolysis, the actual course of reactions has been further modified along the following line:—



Cope (*J. Amer. Chem. Soc.*, 1940, 62, 441) has shown that the condensation of $\alpha\beta$ -unsaturated halides with ethyl alkylidene-cyanoacetate in presence of sodium takes place with the formation of $\beta\gamma$ -unsaturated cyano-ester. During distillation, the unsaturated alkyl groups migrate to the γ -position with regeneration of the $\alpha\beta$ -double bond in the substituted cyano-esters. From a detailed study of the various allied systems, the complete analogy, as well as the genetic relationship of this system with Claisen's rearrangement of phenolic ethers, has been established. The two systems can be represented thus:



Moreover, in the case of Claisen's rearrangement, Δ^2 -cyclohexenyl ether of phenol has been found to migrate to give 2- Δ^2 -cyclohexenyl phenol (Cornforth *et al.*, *J. Proc.*

theoretical amount of dilute sulphuric acid and ice. The alcohol was isolated by steam-distillation and purified from the unchanged halides by heating on the water-bath with freshly heated lime (10 g.). The alcohol passed over at 145°-150°, yield 90 g. This was converted into iodide by treatment with iodine (104 g.), red phosphorous (20 g.) and water (11 c.c.) and refluxing finally for 2 hours. It passed over at 166°-168°, yield 130 g.

Ethyl oxalopropionate was prepared through the condensation of ethyl oxalate with ethyl propionate in presence of sodium ethoxide which on distillation at ordinary pressure gave ethyl methylmalonate in a good yield with loss of carbon monoxide.

Ethyl methylmalonate was converted into the sodium salt by treating with finely divided metal (12.4 g.) under benzene (200 c.c.). *iso*Hexyl iodide (110 g.) was added and the mixture was refluxed on the water-bath for 12 hours and finally in the oil-bath for 10 hours. The desired product distilled at 122°-125°/7 mm., yield 105 g. (Found: C, 64.8; H, 9.8. $C_{14}H_{26}O_4$ requires C, 65.1; H, 10.1 per cent).

α,6-Dimethylheptoic Acid (II).—The above ester was dissolved in rectified spirit (120 c.c.) and to this was added potassium hydroxide (20 g.) in water (20 c.c.) and refluxed for 2 hours. The clear solution was diluted with water, and alcohol was removed on the steam-bath. The neutral matter was extracted with ether and the alkaline solution on acidification gave a crystalline product which was taken up in ether. On removal of the solvent, the residue was rapidly heated to 180°-190° so that the process of decarboxylation was complete within 15 minutes. The residue on distillation in vacuum passed over at 116°/6 mm., yield 21 g.

The acid chloride was prepared by treating the acid (27.5 g.) with PCl_5 (10 c.c.) in the cold. It was left overnight and then refluxed for 3 hours. The acid chloride was decanted off and on distillation it passed over at 79°/9 mm. as a clear, colourless liquid, yield 25 g. The amide, prepared by the interaction of the acid chloride and liquor ammonia, crystallised from dilute acetone, m.p. 96° (cf. Mukherjee, *Science & Culture*, 1941, 7, 59).

ω-Bromomethyl-(1:5-dimethylhexyl)-ketone (III).—The above acid chloride (38 g.) in ether (25 c.c.) was added with cooling to a solution of diazomethane, prepared from nitrosomethylurea (75 g.) in dry ether (500 c.c.). After standing in the cold for an hour, hydrobromic acid (50 c.c., 48%) was slowly added to the yellow solution with constant shaking, when a vigorous evolution of nitrogen took place. The mixture was allowed to stand overnight. The ethereal solution was then washed with water and dilute sodium carbonate solution and dried. On distillation, the bromo-ketone (50.5 g.) was obtained boiling at 103°/9 mm. (cf. Mukherjee, *loc. cit.*). (Found: Br, 33.68. $C_{10}H_{18}OBr$ requires Br, 34.04 per cent).

2-isoHexylheptan-3:6-dione (IV).—Freshly distilled ethyl acetoacetate (21 g.) was added dropwise to a suspension of finely divided sodium (3.4 g.) under ether at 0°. The sodio-salt was cooled further and to this was added the above bromo-ketone (35 g.) dissolved in ether. The product was allowed to stand for 2 days and then refluxed for 4 hours at 50°-55°. It was acidified and extracted with ether, dried and the solvent removed on the water-bath and finally under reduced pressure. The residue, thus obtained, was heated with caustic soda solution (1500 c.c., 2%) at 60° for 5 hours. Next, it was boiled for 10 minutes and on cooling it was extracted thrice with ether.

The alkaline solution was next acidified with hydrochloric acid and warmed on the wire-gauge for 10 minutes until the evolution of gas slackened. On cooling, it was extracted with ether and the ethereal extract was washed with alkali and dried and distilled. The diketone passed over at 122° - 127° /6 mm. as a clear, colourless oil having a characteristic smell, yield 21 g. (Found: C, 74.1, 74.2; H, 10.9, 11.1. $C_{13}H_{24}O_2$ requires C 73.6; H, 11.3 per cent).

2-(2'-Methyl- Δ^2 -cyclopentenyl)-2-carbethoxycyclopentanone (V).—2-Methyl- Δ^2 -cyclopentenol was prepared in a very poor yield from methylcyclopentene by oxidation with selenium dioxide in acetic anhydride solution and subsequent hydrolysis with alkali. The alcohol (5 g.) was diluted with four times its volume of CS_2 and the mixture was thoroughly cooled in ice. PBr_3 (2.5 c.c.) was added dropwise when the solution assumed a deep green colour. It was kept in an ice-chest overnight and then decomposed with ice. Finally the bromide was isolated, b.p. 67° - 75° /20 mm., yield 4 g. It had a characteristic smell producing tears and it rapidly polymerised turning green, and consequently it was immediately used for the next operation.

Ethyl cyclohexanone carboxylate (6 g.) was converted into the potassium salt from potassium (1.1 g.) under xylene and on cooling, the above bromide was added. At first, it was heated on the water-bath for 3 hours and then refluxed in an oil-bath for 7 hours. It was decomposed with water and extracted with ether. On removal of the solvent, the residue was distilled when practically the whole of it came at 130° - 135° /4 mm., yield 4.5 g. (Found: C, 71.6; H, 8.7. $C_{15}H_{22}O_3$ requires C, 72.0; H, 8.8 per cent).

2-(2'-Methyl- Δ^2 -cyclopentenyl)cyclohexanone (VI).—The above product (6 g.) was refluxed with baryta (18 g.), dissolved in distilled water (80 c.c.) for 14 hours. It was cooled and acidified with hydrochloric acid and extracted with ether. After removal of the ether, the residue was distilled in vacuum. A fraction (1 g.) was collected boiling at 115° - 125° /7 mm. and another fraction (2 g.) came over at 215° - 225° /9 mm., which was highly viscous. The latter was not further investigated and the former on distillation, gave the following data, and it was the desired product. (Found: C, 80.2; H, 9.7. $C_{12}H_{18}O$ requires C, 80.8; H, 10.1 per cent).

Ethyl (2'-Methyl- Δ^2 -cyclopentenyl)- Δ^1 -cyclohexenyl-cyanoacetate (VIIa) and/or Ethyl 2-(2'-Methyl- Δ^2 -cyclopentenyl)-cyclohexylidene-cyanoacetate (VIIb).—Ethyl cyclohexylidene-cyanoacetate was prepared through the condensation of ethyl cyanoacetate with cyclohexanone in presence of ammonium acetate, glacial acetic acid and benzene. Sodium (5 g.) was dissolved in dry isopropyl alcohol (25 c.c.) and to this solution, cooled in a freezing mixture, was added ethyl cyclohexylidene-cyanoacetate (4 g.) followed by methylcyclopentenyl bromide (2.4 g.). The mixture was refluxed on the water-bath for 4 hours and in the oil-bath for 6 hours. The product on dilution with water was extracted with ether and the residue, left after evaporation of the solvent, boiled over a wide range, and the fraction passing over at 180° - 200° /7 mm. was collected, yield 3 g. (Found: N, 5.8. $C_{17}H_{23}O_2N$ requires N, 5.2 per cent).

Ethyl 2-cyclohexylcyclopentanone-2-carboxylate (VIII).—To the potassium salt of ethyl cyclopentanone carboxylate, prepared from ethyl cyclopentanone carboxylate (16 g.) and potassium (4 g.) under xylene (30 c.c.) was added cyclohexyl bromide (18 g.) and the mixture was refluxed in an oil-bath for 8 hours. On working up the reaction

water-bath for 12 hours. It was poured into water, extracted with ether and washed with sodium carbonate solution. On distillation, it passed over at 155° - $158^{\circ}/5$ mm., yield 16 g. (Found: C, 68.9. H, 10.4. $C_{18}H_{34}O_4$ requires C, 68.7; H, 10.8 per cent).

Ethyl 3-(1:6-Dimethylhexyl)-cyclopentan-2-one-1-carboxylate (XVI).—The above ester (15 g.) was treated with sodium dust (2.5 g.) in benzene (40 g.) and a few drops of alcohol. It was refluxed for 3 hours when the whole of sodium went into solution. On working up the reaction mixture, the fraction boiling at 140° - $145^{\circ}/3$ mm. was collected, yield 5 g. It gave a very beautiful violet ferric chloride coloration in alcoholic solution. Considerable quantities of a higher boiling residue remained in the flask. (Found: C, 72.1; H, 10.1. $C_{18}H_{34}O_3$ requires C, 71.6; H, 10.4 per cent).

Ethyl 2-(1'-Carbethoxy-2'-keto-3'-1:6-dimethylhexyl) cyclopentenylcyclohexylacetate (XVII).—The above ester (3 g.) was converted into potassium salt by treatment with potassium (0.5 g.) in xylene (10 c.c.) and the unsaturated bromo-ester (XIa, XIb, 5 g.) was added and immediately heated to reflux in an oil-bath. From the reaction mixture, a fraction boiling at 215 - $220^{\circ}/6$ mm. was collected, yield 3.5 g. (Found: C, 72.4; H, 9.1. $C_{26}H_{44}O_5$ requires C, 72.1; H, 9.4 per cent).

The above ester (2 g.) was reduced with Adam's catalyst (0.1 g.) in acetic acid solution, when hydrogen was absorbed very slowly and the reduced ester was isolated at 213° - $216^{\circ}/6$ mm., yield 1.4 g.

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DEPARTMENT OF CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA.

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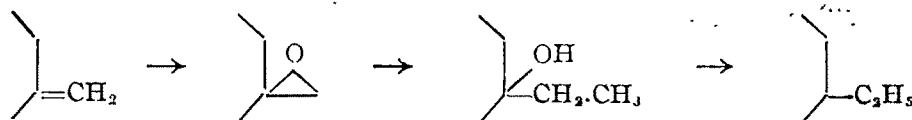
STUDIES IN SESQUITERPENES. PART III. SYNTHESSES OF HOMO-CADALENES

BY SUKH DEV

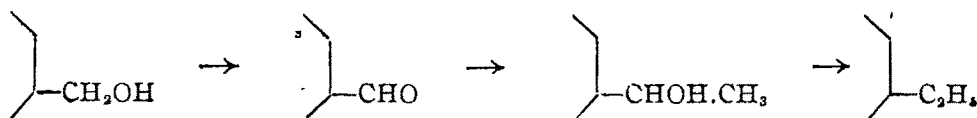
1-Methyl-6-ethyl-4-isopropyl- and 1-ethyl-6-methyl-4-isopropyl-naphthalene have been synthesised.

In the previous part of this series (Sukh Dev, this *Journal*, 1948, 26, 69) it was reported that in connection with our investigations on the sesquiterpenes of the cadinene group it had become necessary to synthesise the then unknown methylcadalenes and the 1-methyl-6-ethyl-4-isopropyl- and 1-ethyl-6-methyl-4-isopropyl-naphthalene. The syntheses of the methylcadalenes were reported there.

In a sesquiterpene of the cadinene type, when an ethylenic linkage is present as a semi-cyclic double bond, the employment of Ruzicka and Sternbach's method for the location of a double bond (*Helv. Chim. Acta*, 1940, 22, 124; cf. Campbell and Soffer, *J. Amer. Chem. Soc.*, 1942, 64, 417; Sukh Dev, *loc. cit.*) may give rise to a homo-cadalene, thus :

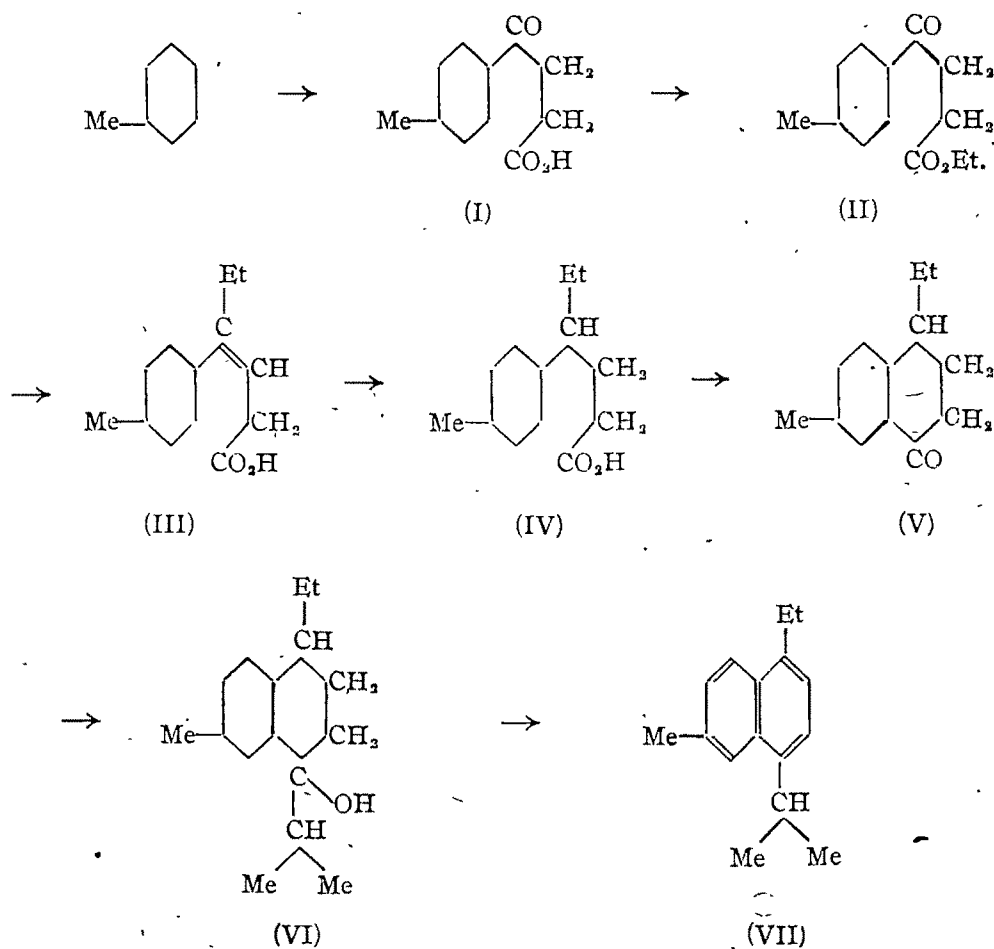


Similarly, a primary alcohol will ultimately give rise to such a hydrocarbon.



With this end in view, 1-methyl-6-ethyl-4-isopropyl- and 1-ethyl-6-methyl-4-isopropyl-naphthalene have been synthesised and their syntheses are reported in the present paper.

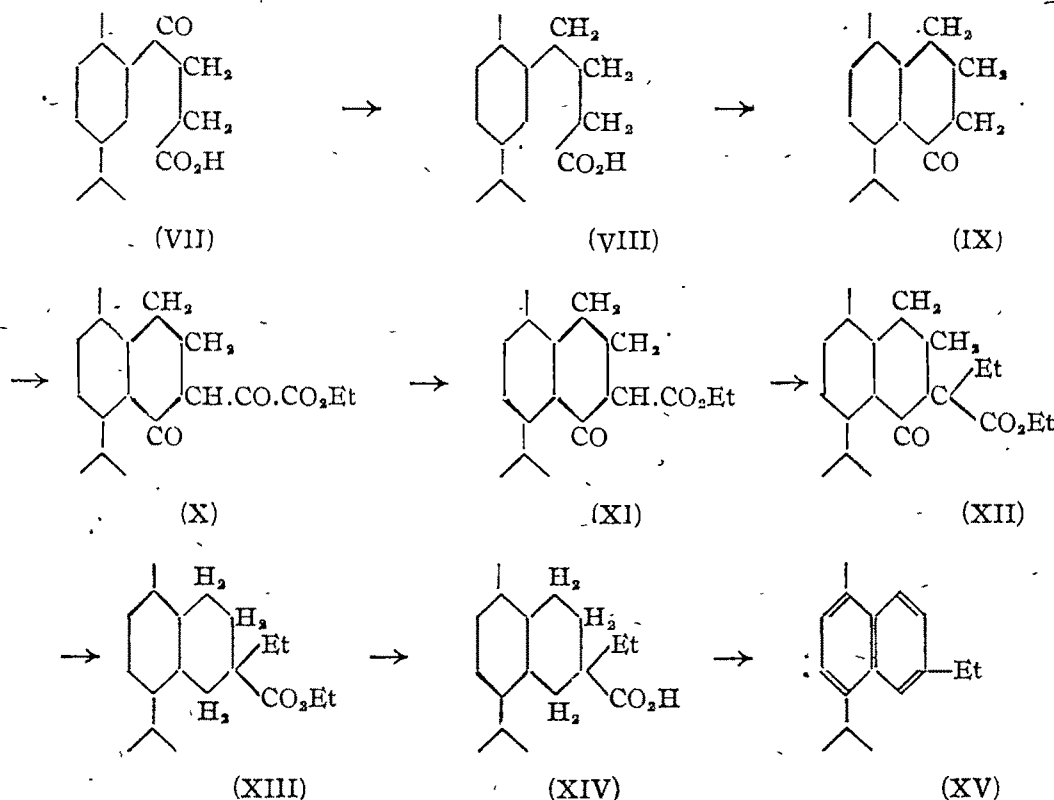
1-Ethyl-6-methyl-4-isopropyl-naphthalene (VII).— β -(*p*-Toluy)propionic acid (I) is prepared by the action of succinic anhydride on toluene in nitrobenzene in the presence of anhydrous aluminium chloride (cf. Barnett and Sanders, *J. Chem. Soc.*, 1933, 434). Its ethyl ester (II) is treated with ethyl magnesium bromide, when γ -(*p*-tolyl)- γ -ethylvinylacetic acid (III) is obtained in a good yield. The acid is reduced with hydroiodic acid and red phosphorus giving γ -(*p*-tolyl)- γ -ethylbutyric acid (IV). This substance has been prepared previously by Brunner and Grof (*Monatsh*, 1934, 64, 28). Their synthesis starts from 4-methylpropionophenone and is a lengthy one involving eight operations, whereas the present scheme gives much better overall yields and employs only four steps.



The acid is next cyclised with anhydrous aluminium chloride using the technique recommended by Sukh Dev and Guha (this *Journal*, 1948, **25**, 38; also Sukh Dev, *loc. cit.*) for the ring-closure of compounds of similar structure. The tetralone (V) is obtained in a yield of 91%. Brunner and Grof (*loc. cit.*) obtained a yield of 74.6% based on the weight of pure acid chloride using anhydrous aluminium chloride. The same authors have also employed the sulphuric acid method and prepared the ketone in 61.6% yield. By the action of magnesium isopropyl bromide on 7-methyl-4-ethyltetralone-1 an unstable carbinol (VI) is obtained, which is dehydrated with 90% formic acid and then dehydrogenated with selenium to give the required homo-cadalene (VII).

1-Methyl-6-ethyl-4-isopropyl-naphthalene (XV).—5-Methyl-8-isopropyltetralone-1 (IX) is prepared by the cyclisation of γ -(*p*-cymyl-2)-butyric acid (VIII) (Sukh Dev and Guha, *loc. cit.*). The ketone is condensed with ethyl oxalate in the presence of sodium ethoxide yielding ethyl 1-keto-5-methyl-8-isopropyl-1:2:3:4-tetrahydronaphthalene-2-glyoxalate (X) (cf. Bachmann, Cole and Wilds, *J. Amer. Chem. Soc.*, 1940, **62**, 831; Bachmann and Thomas, *ibid.*, 1941, **63**, 599; Bachmann and Wendler, *ibid.*, 1946, **68**, 2583). The crude glyoxalate is decomposed using the procedure of Bachmann, Cole and

Wilds (*loc. cit.*) Ethyl-1-keto-1:2:3:4-tetrahydro-5-methyl-8-isopropyl-2-naphthoate (XI), thus obtained, is converted into the sodium salt and treated with ethyl bromide giving (XII) (cf. Kloetzel and Close, *J. Org. Chem.*, 1946, **11**, 396).



The hydrolysis of such β -keto-esters has been carried out both by acids and alkalis (Titley, *J. Chem. Soc.*, 1928, 2578; Campbell and Soffer, *J. Amer. Chem. Soc.*, 1942, **64**, 423; Bachmann, Cole and Wilds, *ibid.*, 1940, **62**, 832; Kloetzel, *ibid.*, 1940, **62**, 1711; Kloetzel and Close, *loc. cit.*). Titley (*loc. cit.*) reported that 2-methyl-2-carboethoxy-tetralone-1 on alkaline hydrolysis gave a mixture of 2-methyltetralone-1 and γ -o-carboxypnenyl- α -methylbutyric acid, whereas on hydrolysis with 20% sulphuric acid the tetralone was obtained in a quantitative yield. For our compound (XII) we selected the acid hydrolysis with 20% sulphuric acid, but even after refluxing for 15 hours, the ester was isolated unchanged. It was decided not to submit this β -keto-ester, which is so resistant to hydrolysis, to a prolonged treatment with hot alkali to avoid ring fission. Hence the keto-ester was subjected to Clemmensen reduction (Martin's modification) for 36 hours; ethyl 2-ethyl-5-methyl-8-isopropyl-1:2:3:4-tetrahydro-2-naphthoate (XIII) was obtained in an excellent yield. Curiously enough, the ester grouping remained intact. Though an ester grouping on a quaternary carbon atom is eliminated on selenium dehydrogenation (Ruzicka and Meyer, *Helv. Chim. Acta*, 1922, **5**, 581; Bardhan and Sengupta, *J. Chem. Soc.*, 1932, 2520, 2798), the compound is hydrolysed with alcoholic sodium hydroxide. The acid (XIV) is isolated in a good yield which on

dehydrogenation with selenium gives the required 1-methyl-6-ethyl-4-isopropyl-naphthalene, the carboxyl group being eliminated during the reaction (cf. Diels and Karstens, *Ber.*, 1927, **60**, 2323; Darzens and Levy, *Compt. rend.*, 1934, **199**, 1131; 1935, **201**, 730; 1936, **202**, 427).

The melting points of the derivatives of these two hydrocarbons together with those of the methylcadalene derivatives are tabulated below :

TABLE I.

Hydrocarbon.	B. p.	Picrate, m. p.	Styphnate, m. p.	T. N. B. compd., m. p.	T. N. T. compd., m. p.
Cadalene	—	—	—	—	—
2-Methyl*	—	143-44°	170-71°	168-69°	—
3-Methyl	126°-130°/2 mm.	162-63°	—	165°	—
5-Methyl	132°/1.5 mm. 140°-145°/3 mm.	102.5-103.5°	130-31°	160-61°	87-88°
7-Methyl*	—	122-23°	—	—	—
8-Methyl	144°-147°/3 mm.	108-8.5°	—	118-18.5°	—
1-Ethyl-6-methyl- 4-isopropyl- naphthalene	134°-140°/2 mm.	—	—	92°	—
1-Methyl-6-ethyl- 4-isopropyl- naphthalene	126°-127°/1 mm.	—	—	85.5-86.5°	—

* Campell and Soffer, *J. Amer. Chem. Soc.*, 1942, **64**, 417.

EXPERIMENTAL

1-Ethyl-6-methyl-4-isopropyl-naphthalene (VII)

β-(*p*-Tolyl)-*propionic Acid* (I).—Succinic anhydride (30.0 g., 1 mol.) was condensed with toluene (30.6 g., 1.1 mol.) in dry nitrobenzene (150 c. c.) in the presence of anhydrous aluminium chloride (89.1 g., 2.2 mols.). The details as given for the preparation of *β*-(*p*-cymoyl)-*α*-methylpropionic acid (Sukh Dev and Guba, *loc. cit.*) were followed. Yield of the crude product, m. p. 121-24°, was quantitative. The crude product was dissolved in 3 parts of dry benzene and one part of petrol (b. p. 60°-80°) was added and the product was allowed to crystallise during several hours when it was obtained as colourless lustrous plates, m. p. 129-30°, yield 52 g. (90%). Barnett and Sanders (*loc. cit.*) give the m. p. as 129°.

Ethyl β-(*p*-Tolyl)-*propionate* (II).—The acid (45 g.), alcohol (95%, 135 c. c.) and concentrated sulphuric acid (6 c. c.) were refluxed for 7 hours. The reaction mixture was cooled, diluted with water and neutralised with sodium carbonate. The ester crystallised out slowly, when it was filtered off. The crude product was carefully crystallised from dilute alcohol in colourless, long needles, m. p. 42-43.5°, yield 47 g. (91%). Rupe and Steinbach (*Ber.*, 1911, **44**, 584) report the m. p. as 42-43°.

γ-(*p*-Tolyl)-*γ*-ethylvinylacetic Acid (III).—A Grignard reagent was prepared from magnesium (2.2 g., 0.085 M), ethyl bromide (8 c. c., 0.1 M) and dry ether (35 c. c.). Ethyl *β*-(*p*-tolyl)-*propionate* (11 g., 0.05 M) was dissolved in dry ether (75 c. c.) and the

inverse Grignard reaction was carried out by following the details as given for the preparation of γ -(*p*-tolyl)- γ -dimethylvinylacetic acid (Sukh Dev, *loc. cit.*). The crude product was obtained as a thick reddish yellow oil in 75% yield.

Sometimes, in such reactions, if due to some reason the neutral fraction forms a considerable part of the reaction product, the β -aroyl propionic acid (present as the ester) may be separated from the $\beta\gamma$ -unsaturated acid (present as the lactone or the ester) by the following method :

The crude neutral fraction is hydrolysed with alcoholic alkali (3-4 hrs.), most of the alcohol is then distilled off and the product diluted with water and extracted with ether to remove any neutral portion. The alkaline solution is clarified with norit and acidified with hydrochloric acid (Congo red); the product (solid or oil) is separated and digested with dilute hydrochloric (1:1) on the water-bath for 2 hours. This treatment converts unsaturated acid into the lactone, whereas the keto-acid remains unaffected. The product is then taken up in ether and separated into acid and neutral fractions with sodium carbonate solution. The acid part will consist chiefly of β -aroyl propionic acid, while the neutral fraction will contain the lactone of the corresponding $\beta\gamma$ -unsaturated acid, which can be submitted to hydroiodic acid reduction as such. The method has been used successfully.

γ -(*p*-Tolyl)- γ -ethylbutyric Acid (IV).—The crude unsaturated acid (21.0 g.), hydriodic acid (d 1.7, 105 g.) and red phosphorus (14 g.) were refluxed in an oil-bath at 130°-140° for 24 hours and worked up in the usual manner. The product was purified by distillation in vacuum. The acid was obtained as a colourless, viscous liquid, b. p. 158°/1 mm. in a yield of 66.6% (14 g.). Brunner and Grof (*loc. cit.*) report b. p. as 189°/13 mm.

4-Ethyl-7-methyltetralone-1 (V).— γ -(*p*-Tolyl)- γ -ethylbutyric acid (12 g., 1 mol.) in dry benzene (25 c. c.) was converted into the acid chloride by PCl_5 (13.5 g., 1.1 mol., covered with 25 c. c. of dry benzene) in the usual manner and the acid chloride without being purified was cyclised by anhydrous aluminium chloride (8.5 g., 1.1 mol.). The details as given for the cyclisation of γ -(*p*-cymyl-2)- α -methylbutyric acid (Sukh Dev and Guha, *loc. cit.*) were followed. The reaction proper was complete in about $\frac{1}{2}$ hour. The product was purified by distillation in vacuum and obtained as a colourless, mobile liquid, b. p. 130°-131°/1 mm., yield 10 g. (91%). Brunner and Grof. (*loc. cit.*) give the b. p. as 159°/11 mm. (Found : C, 82.30; H, 8.41. $\text{C}_{15}\text{H}_{16}\text{O}$ requires C, 82.97; H, 8.51 per cent).

The *semicarbazone* was prepared in the usual manner and crystallised from alcohol as colourless, small plates, m. p. 162-63° Brunner and Grof (*loc. cit.*) record 156° as the m. p.

1-Ethyl-6-methyl-4-isopropylnaphthalene (VII).—*iso*Propyl magnesium bromide (prepared from magnesium 1.9 g., *iso*propyl bromide, 8 c. c. and dry ether, 50 c. c.) was reacted with the above tetralone (9 g. in 45 c. c. of dry ether) in the same way as described under 1:3:6-trimethyl-4-isopropylnaphthalene (Sukh Dev, *loc. cit.*).

The crude carbinol (10 g.), which was obtained as a viscous yellow liquid, was dehydrated with 90% formic acid (20 c. c.) by heating on a water-bath for 3 hours. The product was worked up as usual and fractionated in vacuum, when 6.0 g. (55%) of a colourless, mobile liquid, b. p. 122°-130°/1 mm. were obtained.

The hydrocarbon was dehydrogenated with selenium (3 g.) in a potassium nitrate-sodium nitrite bath. The reaction started at 300° and was quite brisk. The heating was carried out at 310° for 24 hours when the evolution of hydrogen selenide had practically stopped. The product was isolated in the usual manner and purified by repeated distillations over sodium. The required naphthalene was obtained as a colourless, mobile liquid, b. p. 134°-140°/2 mm. in 60% yield (3.6 g.). (Found : C, 92.53, 92.36; H, 8.76, 8.97. $C_{16}H_{10}$ requires C, 90.56, H, 9.43 per cent.).

The T. N. B. Compound.—The hydrocarbon (0.5 g.) was added to a hot solution of 0.5 g. of T. N. B. in 10 c. c. of alcohol and allowed to crystallise slowly. The product was once crystallised from 80% acetic acid and again from alcohol till the m. p. could not be raised further. It was obtained from alcohol as bright yellow needles, m. p. 92°.

1-Methyl-6-ethyl-4-isopropynaphthalene (XV)

5-Methyl-8-isopropyltetralone-1 (IX) was prepared by the cyclisation of γ -(*p*-cymyl-2)-butyric acid, obtained by the Clemmensen reduction (Martin's modification) of β -(*p*-cymoyl-2)-propionic acid, which was synthesised from *p*-cymene and succinic anhydride in the presence of aluminium chloride. Details for these have been given under the synthesis of apo-cadalene (Sukh Dev and Guha, *loc. cit.*).

Ethyl 1-Keto-5-methyl-8-isopropyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-glyoxalate (X).—Such compounds have been prepared by the condensation of cyclic ketones with oxalic esters in the presence of sodium ethoxide or sodium methoxide. Bachmann *et al.* (*loc. cit.*) have mostly used dimethyl oxalate and have employed sodium methoxide as the condensing agent. The reactions have been carried out in an atmosphere of nitrogen. This condensation, however, was conducted as follows :

Dry sodium ethoxide prepared from sodium (3.45 g., 0.15 M) and absolute alcohol (60 c. c.), followed by removal of excess alcohol in vacuum at 100°, was suspended in 80 c. c. of dry benzene with swirling. The suspension was cooled in ice-water mixture and a solution of tetralone (15 g., 0.075M) and diethyl oxalate (21.9 g., 0.15 M) in 30 c. c. of dry benzene was added with swirling and cooling. The mixture was swirled in the ice-bath for some time till practically all the sodium ethoxide had disappeared and a clear brownish yellow solution was obtained. The reaction mixture was kept at the room temperature (24°) for 6 hours (CaCl₂-sodalime guard tube) and was then poured on to ice. 5% Potassium hydroxide solution (50 c. c.) was added, and shaken well and the aqueous layer was separated. The benzene layer was extracted twice with 2% aqueous potash and the alkaline extracts were mixed and acidified with hydrochloric acid. An oil separated which was taken up in ether and the solution was dried (MgSO₄) and the solvent removed, when 22 g. (98%) of a dark, slightly viscous oil were left.

Ethyl 1-Keto-1 : 2 : 3 : 4-tetrahydro-5-methyl-8-isopropyl-2-naphthoate (XI).—The crude glyoxalate (22 g.) and fine, soft glass powder (10 g.) were heated together in an oil-bath at 160°-170° with occasional stirring till all the carbon monoxide had been evolved (2 hrs.). The reaction mixture was cooled, diluted with a little ether and the product decanted off from the glass powder. The solvent was removed and the product was distilled in vacuum, when the keto-ester was obtained as a colourless, viscous liquid,

b. p. 170° - 172° /1 mm., yield 15 g. (75% overall yield based on the weight of the tetralone employed). (Found: C, 75.32; H, 8.04. $C_{17}H_{22}O_3$ requires C, 74.45; H, 8.03 per cent).

The product gives an intense green coloration with alcoholic ferric chloride. With concentrated sulphuric acid a deep yellow colour is obtained. A solution of bromine in chloroform is also decolourised.

Ethyl 1-Keto-1: 2: 3: 4-tetrahydro-5-methyl-2-ethyl-8-isopropyl-2-naphthoate (XII).—For the alkylation of β -keto-esters of a similar structure, some workers have used one mole of sodium for one mole of the ester (e. g. Titley, *loc. cit.*), whereas others (Bachmann *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 832; 1941, **63**, 598; Kloetzel, *loc. cit.*; Kloetzel and Close, *loc. cit.*) have employed 4 moles of sodium for one mole of the keto-ester and have used the alkyl halide in large excess. These latter workers have obtained the alkylated products in very good yields. For our reaction, we have used 1.5 mole of sodium, but the alkylation was not complete, as some 5-methyl-8-isopropyltetralone-1 was isolated on hydrolysis. Hence, it will be profitable to use the method employed by Bachmann and co-workers. Kloetzel and Close (*loc. cit.*) during the ethylation of 2-carbomethoxy-1-tetralone found that ethyl bromide gave erratic results, whereas ethyl iodide worked smoothly. However, for our ethylation, we have employed ethyl bromide.

Sodium (1.8 g., 0.075 M) was dissolved in absolute alcohol (40 c. c.) in a dry reflux apparatus carrying a calcium chloride-sodalime guard tube. The solution was cooled and the ester (13.7 g., 0.05 M) dissolved in dry benzene (40 c. c.), was added. The mixture was refluxed for $\frac{1}{2}$ hour, cooled and ethyl bromide (10.9 g., 0.1 M) introduced. The reaction mixture was kept at room temperature for 2 hours and it was then refluxed for 45 minutes and left overnight. A lot of sodium bromide had separated out. The product was cooled, just neutralised with acetic acid and the solvents were removed by distillation, the last traces being removed in vacuum at 100° .

It was attempted to hydrolyse the crude ethylated product: To the residue containing the crude alkylated β -ketonic ester, 20% sulphuric acid (100 c. c.) and glacial acetic acid (10 c. c.) were added. The mixture was refluxed in an oil-bath at 130° - 140° for 15 hours and was then worked up in the usual manner. The product was fractionated in vacuum. The first fraction of b. p. 165° - 170° /10 mm. (yield 3.0 g.) was identified to be 5-methyl-8-isopropyltetralone-1, by its 2:4-dinitrophenylhydrazone, m. p. 198.5 - 99.5° . (mixed m. p. with an authentic sample). The rest of the product was distilled in high vacuum (2nd fraction), when the distillate crystallised out. This was recrystallised from alcohol as colourless, stout, well-developed prisms, m. p. 69.5 - 70.5° , yield 7 g. The product neither gave a coloration with alcoholic ferric chloride nor a 2:4-dinitrophenylhydrazone. (Found: C, 74.69, 74.71; H, 8.45, 8.46. $C_{19}H_{22}O_3$ requires C, 75.5; H, 8.6 per cent).

Ethyl 1: 2: 3: 4-Tetrahydro-5-methyl-2-ethyl-8-isopropyl-2-naphthoate (XIII).—Zinc amalgam was prepared from zinc wool (15 g.), mercuric chloride (1.5 g.), concentrated hydrochloric acid (0.8 c. c.) and water (22 c. c.). Water, etc. were decanted off the amalgamated zinc and water (12 c. c.), concentrated hydrochloric acid (27 c. c.), toluene (15 c. c.) and the keto-ester (5 g.) were added in the order indicated. A few drops of glacial acetic acid were added and the reaction mixture was refluxed for 36

hours in an oil-bath at 120° - 140° . After every 6 hours, 10 c. c. of concentrated hydrochloric acid were being added. The product was worked up in the usual manner and distilled in vacuum as colourless, slightly viscous liquid, b. p. 164° - $168^{\circ}/5$ mm., yield 4 g. (89.5%). (Found : C, 79.11; H, 9.59. $C_{16}H_{14}O_2$ requires C, 79.16; H, 9.72 per cent).

1-Methyl-6-ethyl-4-isopropyl-naphthalene (XV).—The ester (4.0 g.) was refluxed with alcoholic sodium hydroxide (3.6 g. of alkali in 30 c. c. of alcohol) for 32 hours. The product was cooled, diluted with water and once extracted with ether to remove any neutral substance and then acidified (Congo red) with dilute hydrochloric acid. An oil separated which solidified on standing overnight. Yield of the crude product of m. p. 97 - 98° was 3.6 g. (97.3%).

The crude acid (3.5 g.) and selenium (5 g.) were heated together in a potassium nitrate-sodium nitrite bath at 300° - 330° for 48 hours. The product was worked up in the usual manner and purified by distillation over sodium as colourless, mobile liquid, b. p. 126° - $127^{\circ}/1$ mm., yield 50%. (Found : C, 90.69; H, 9.19. $C_{18}H_{20}$ requires C, 90.56 H, 9.43 per cent).

The *trinitrobenzene* compound was prepared by adding 0.5 g. of the hydrocarbon to T. N. B. (0.5 g.) in boiling alcohol (10 c. c.). The crystals which separated were recrystallised to a constant m. p. from alcohol. The product separated as bright, canary yellow needles, m. p. 85.5 - 86.5° . Mixed m. p. with the T. N. B. compound of (VII), (m. p. 92°) was 75 - 77° with previous shrinkage.

These two hydrocarbons (VII and XV) described in this paper yield derivatives which are quite soluble in alcohol as compared to those of the methylcadalenes. The picrates are much more soluble than the T. N. B. compounds and hence are not recommended for characterisation purposes.

The thanks of the author are due to Prof. P. C. Guha for the kind interest he has taken in this investigation.

ORGANIC CHEMISTRY LABORATORIES,
DEPARTMENT OF PURE AND APPLIED CHEMISTRY,
INDIAN INSTITUTE OF SCIENCE, BANGALORE.

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STUDIES IN SESQUITERPENES. PART IV. HYDRIODIC ACID FOR
SIMULTANEOUS RING-CLOSURE AND REDUCTIONS :
SYNTHESIS OF ALKYL NAPHTHALENES

By SUKH DEV

New syntheses of some alkyl naphthalenes involving simultaneous ring-closure and reductions by hydriodic acid are reported.

In the synthesis of various alkyl naphthalenes, very often, a γ -aryl butyric acid, obtained through a series of reactions, is subjected to intramolecular condensation to obtain the corresponding tetralone, which in turn is reduced to yield a hydrocarbon ; the latter on dehydrogenation furnishes the required naphthalene (Harvey, Heilbron and Wilkinson, *J. Chem. Soc.*, 1930, 423, 2537 ; Wilkinson, 1931, 1333 ; Ruzicka *et al.*, *Helv. Chim. Acta*, 1932, 15, 140 ; 1933, 16, 314 ; 1936, 19, 370 ; Barnett and Sanders, *J. Chem. Soc.*, 1933, 434 ; Rapson and Short, *ibid.*, 1933, 128 ; Brunner and Grof, *Monatsh.*, 1934, 65, 28 ; Sukh Dev and Guha, *J. Indian Chem. Soc.*, 1948, 25, 38 *et seq.*). Sometimes the final production of the aryl butyric acid is preceded by the reduction of the corresponding $\beta\gamma$ -unsaturated acid, obtained by the action of alkyl magnesium halide on methyl β -aroyle-propionate.

A method has now been developed which completes all the three steps, viz. reduction, ring-closure and further reduction, in one operation.

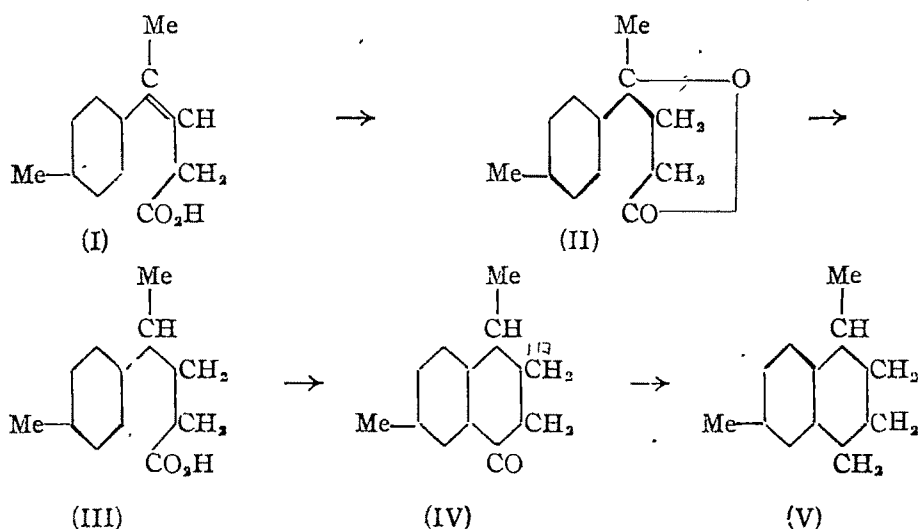
During the synthesis of 1:3:6-trimethyl-4-isopropyl-naphthalene (3-methylcadalene) (Sukh Dev, this *Journal*, 1948, 25, 70) γ -(*p*-tolyl)- γ -dimethylvinylacetic acid was subjected to reduction with hydriodic acid and red phosphorus. It was observed that besides the normal reduction product, γ -(*p*-tolyl)- γ -dimethylbutyric acid, a neutral fraction was always obtained. The amount of this neutral fraction depended on the time for which the reaction mixture had been refluxed. In one instance (40 hours' refluxing) this formed the chief product (75%). On analysis, the neutral fraction was found to consist of 2:4:7-trimethyltetralone-1 (50%) and 1:3:6-trimethyl-1:2:3:4-tetrahydronaphthalene (50%). Further work on this observation was taken up in order to work out conditions under which satisfactory yields of the tetrahydronaphthalene should be obtained. This has been accomplished.

A few not very dissimilar instances are recorded in the literature. Thus Ullmann (*Annalen*, 1896, 291, 19) obtained dihydroanthracene by the reduction of *o*-benzoylbenzoic acid with HI and red phosphorus. α -Tetralone was identified by Miescher and Billeter (*Helv. Chim. Acta*, 1939, 22, 605) as a minor product of the reduction of β -benzoylpropionic acid with potassium iodide and red phosphorus in syrupy phosphoric acid. Scholl and co-workers (*Ber.*, 1932, 65, 1398 ; 1936, 69, 707) used acetic anhydride containing hydriodic acid in the preparation of anthranil acetates from some *o*-arylbenzoic acids.

A number of experiments were carried out on γ -(*p*-tolyl) butyric acid, using hydriodic acid and red phosphorus, and Miescher and Billeter's modification (*loc. cit.*) of the hydriodic acid reduction. Best results are obtained by heating the butyric acid with iodine and red phosphorus in syrupy phosphoric acid for 48 to 60 hours in an oil-bath

at 160°-170°. 6-Methyl-1:2:3:4-tetrahydronaphthalene was obtained in yields of 70 to 75%. The method was then applied to a number of other butyric acids and good results were obtained. γ -Aryl-butyric acids with a methyl radical in the α -position give better results. This may, in part, be due to the effect of the methyl group on the cyclisation of the acid (Mayer and Stamm, *Ber.*, 1923, 56, 1424).

The reaction proceeds in a straight forward manner. The butyric acid first undergoes cyclisation to give the tetralone, which in turn is reduced to the hydrocarbon. In the case of the corresponding vinylacetic acids, the unsaturated acid is first lactonised under the influence of the acids; the lactone ring is then broken up by hydriodic acid producing the butyric acid. For example, when γ -(*p*-tolyl)- γ -methylvinylacetic acid (I) is subjected to this treatment, the reaction takes the following course :



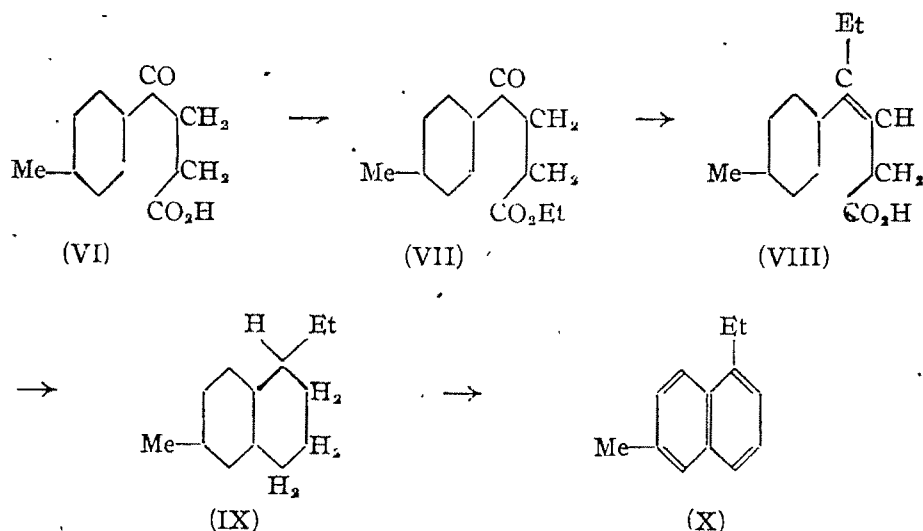
The different products of the reaction can be isolated at different stages. By refluxing (I) with hydriodic acid and red phosphorus for 3 hours at 130°-140° the lactone (II) can be isolated in yields of 65-75%, which is known to produce the butyric acid (III) on reduction with hydriodic acid and red phosphorus (Rupe and Steinbach, *Ber.*, 1911, 44, 585). The acid (III) can give rise to (IV) and (V) in varying amounts depending on the time for which the reaction is to be carried out. By a prolonged treatment, (V), practically free from the tetralone, can be produced. The mechanism of the ring-closure is obscure, may be it is a case of simple dehydration.

Though the reaction has the disadvantage of requiring a comparatively long period of refluxing, this is readily counterbalanced by the simplicity of the reaction, no special attention being necessary. Moreover, the overall yields are better and the hydrocarbon is produced in a more or less pure state. Practically no coloured byproducts and resins are produced.

The method has been applied to the synthesis of a number of known alkyl naphthalenes.

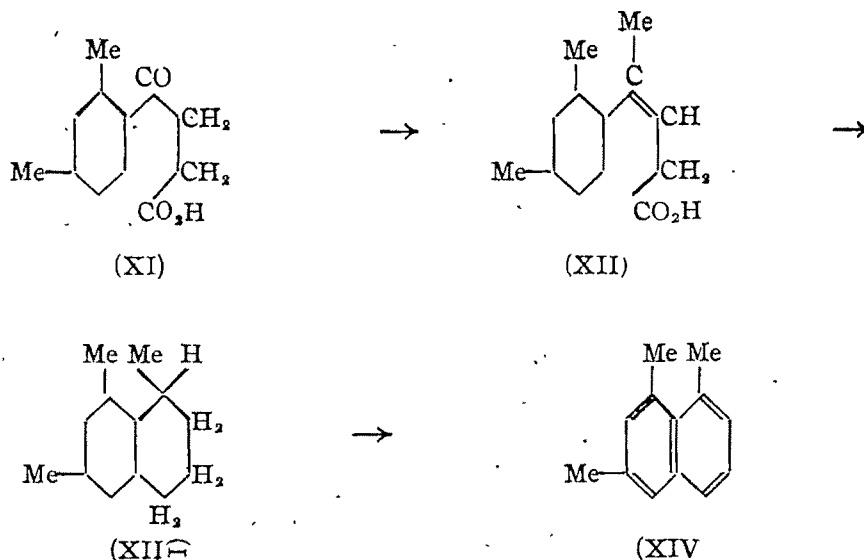
1-Ethyl-6-methylnaphthalene (X).—The hydrocarbon has been synthesised previously by Brunner and Grof (*loc. cit.*). Their starting material was *p*-methylpropiophenone,

which was converted into the naphthalene after nine steps. The present scheme is outlined below.



γ -(*p*-Tolyl)- γ -ethylvinylacetic acid (VIII) was generated from ethyl β -(*p*-toluyl)-propionate (VII) by the action of ethyl magnesium bromide (Sukh Dev, this *issue*, p. 315). This acid on treatment according to the present method gave 6-methyl-4-ethyl-1:2:3:4-tetrahydronaphthalene (IX). The hydrocarbon on dehydrogenation with sulphur furnished the naphthalene (X).

1:3:8-Trimethylnaphthalene (XIV).— γ -(2-*m*-Xylyl)- γ -methylvinylacetic acid (XII) was prepared from β -(2-*m*-xyloyl)-propionic acid (XI) by the method of Sukh Dev (*loc. cit.*). The unsaturated acid on treatment with iodine and red phosphorus in syrupy phosphoric acid furnished the tetrahydronaphthalene (XIII), which on dehydrogenation with sulphur gave the compound (XIV).



Other Alkyl Naphthalenes

βγ-Unsaturated acids (VIII, XII and XVI) were obtained by the action of alkyl magnesium halide on the methyl *β*-aroyl-propionates. (For details see the references quoted).

Tetrahydronaphthalenes (IX, XIII and XVII).—The reaction was carried out as described under 1:6-dimethylnaphthalene. 1-Ethyl-6-methyl-1:2:3:4-tetrahydronaphthalene (IX) was obtained as a colourless, mobile liquid, b. p. 118°/6 mm., yield 70.0%. (Brunner and Grof, *loc. cit.* give b. p. 126°/10 mm.)

1:6:8-Trimethyl-1:2:3:4-tetrahydronaphthalene (XIII) was obtained in a yield of 65-75%, b. p. 125-126°/9 mm. (Heilbron and Wilkinson, *loc. cit.* give b. p. 133°-136°/18.5 mm.).

1:3:6-Trimethyl-1:2:3:4-tetrahydronaphthalene (XVII), b. p. 110°-114°/5 mm. was isolated in a yield of 80%.

Naphthalenes (X, XIV and XVIII).—The above tetrahydronaphthalenes were dehydrogenated with sulphur, as described under *β*-methylnaphthalene. The hydrocarbons were purified by distillation over sodium and characterised by the preparation of suitable derivatives. All derivatives were recrystallised till the melting points could not be raised further. The melting points of these derivatives, as recorded in the literature, are given in Table I.

1-Ethyl-6-methylnaphthalene (X) was obtained as a colourless, mobile liquid, b. p. 118°/4 mm. Brunner and Grof (*loc. cit.*) give b. p. 135°-138°/12 mm. The picrate crystallised from alcohol in small, silky, yellow needles, m. p. 82°.

1:3:8-Trimethylnaphthalene (XII) crystallised from alcohol in plates, m. p. 47-48°. Heilbron and Wilkinson (*loc. cit.*) give m. p. 48°. The picrate was obtained as deep orange needles from alcohol, m. p. 125-26°.

1:3:6-Trimethylnaphthalene (XVIII) b. p. 115°-120°/3 mm. was obtained in a yield of 75%. Ruzicka and Ehmman (*loc. cit.*) give b. p. 140°-144°/10 mm. The picrate crystallised from alcohol in orange-red needles, m. p. 115°. The styphnate was obtained as yellow silky needles, m. p. 126°.

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ORGANIC CHEMISTRY LABORATORIES,
DEPARTMENT OF PURE & APPLIED CHEMISTRY,
INDIAN INSTITUTE OF SCIENCE, BANGALORE.

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CRYSTALLINE COMPONENTS OF THE BARK OF *PRUNUS PUDDUM*, ROXB. PART III

BY DUHKHAHARAN CHAKRAVARTI, NAKULESWAR KUNDU AND RANJIT PRASAD GHOSH

The compound, m. p. 150-52°, isolated from *Prunus puddum*, has been shown to contain the flavanone sakuranetin (m. p. 152°) along with traces of another compound (m. p. 198-200°). Diacetyl sakuranetin (m. p. 166-68°) has been described. The acetyl derivative of sakuranetin (m. p. 97°) described by Asahina and co-workers seems to be an impure substance.

A hard, shining, colourless crystalline solid (m. p. 150-52°) has been isolated from the bark of *Prunus puddum* Roxb. (N. O. Rosaceae) (Chakravarti and Ghosh, *J. Indian Chem. Soc.*, 1944, **21**, 173). This compound (C₁₆H₁₄O₆) shows identical colour reactions as the flavanone, sakuranetin (I) (Asahina, *Arch. Pharm.*, 1908, **246**, 259; Asahina, Shinoda and Inubuse, *J. Pharm. Soc.*, Japan, 1927, No. 550, p. 133; 1928, No. 553, p. 29) and some of its derivatives are also similar to the derivatives of sakuranetin, but the methoxyl value is much higher than that required by sakuranetin. Further, it does not form the acetyl derivative (m. p. 97°) described by Asahina and co-workers (*ibid.*, 1927).

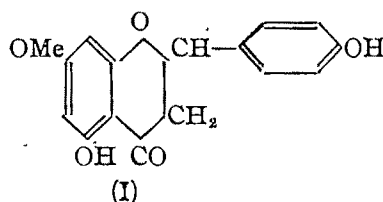


TABLE I

	Compound (m. p. 150-52°).	Sakuranetin (m. p. 152°).
Coloration with ferric chloride	Violet	Violet
Coloration with fuming nitric acid	Indigo-blue rapidly changed to violet	Indigo-blue rapidly changed to violet
Coloration with magnesium powder and hydrochloric acid	Pinkish violet which deepens gradually	Pinkish violet which deepens gradually
Tetramethyl ether	Yellow plates, m. p. 119°	Yellow plates, m. p. 119°
Dimethyl ether	Colourless needles, m. p. 116-17°	Colourless needles, m. p. 116°
Triacetyl derivative	Colourless prisms, m. p. 144-46°	Colourless prisms, m. p. 145°
Oxime	Colourless needles, m. p. 198-200°	Colourless needles, m. p. 198-200°

The melting point of the compound does not rise on repeated crystallisations from different solvents. On high vacuum distillation it distils at 195°-205°/0.5 mm. and at

165°/0.2 mm., but the methoxyl content of the distilled product is still much higher than that required for sakuranetin.

The substance has been acetylated under various conditions and the different acetyl derivatives deacetylated with interesting results. With acetic anhydride and concentrated sulphuric acid, a gummy product is obtained, which could not be crystallised. Attempts to prepare the acetyl derivative (m. p. 97°) described by Asahina have been unsuccessful.

When a few drops of pyridine are used as a condensing agent, a small amount of well defined needles, m. p. 145°, is obtained; the melting point is the same as that of triacetyl sakuranetin (2:6:4'-triacetyl-4 methoxychalkone) described by Asahina and his co-workers (*ibid.*, 1928).

When acetylated with acetic anhydride in the presence of freshly fused sodium acetate, three distinct products are isolated.

(i) The acetyl derivative, m. p. 144-46°, evidently triacetyl sakuranetin, which on deacetylation with 15% sulphuric acid gives the original substance, m. p. 150-51°. This deacetylated product has the methoxyl content as required by sakuranetin.

(ii) An acetyl derivative, m. p. 166-68°, which on deacetylation also gives the original substance, m. p. 151°. The analytical data show that it is the diacetyl derivative of sakuranetin. This has not been described by Asahina and the acetyl derivative (m. p. 97°), obtained by him by acetylation in presence of sulphuric acid, appears to be an impure substance. It gives a pink colour with magnesium powder and hydrochloric acid.

(iii) A very small quantity of the acetyl derivative, m. p. 214-16°. On deacetylation, it gives a compound, m. p. 198-200°. It does not give any coloration with ferric chloride, but with magnesium powder and hydrochloric acid it gives a pink colour.

Thus, it is found that the substance, m. p. 150-52°, is not pure sakuranetin but a mixture of two compounds, *e.g.*, (1) sakuranetin, m. p. 152° and (2) unknown compound, m. p. 198-200°.

Mahal, Rai and Venkataraman (*J. Chem. Soc.*, 1935, 866; 1936, 569) and Chakravarti and Datta (*J. Indian Chem. Soc.*, 1939, 16, 639) have observed that certain flavanones or even some chalkones are oxidised by selenium dioxide smoothly to give rise to flavones. It was expected that oxidation of sakuranetin with selenium dioxide would lead to puddumetin (Genkawanin) isolated from the same plant (Chakravarti and Ghosh, *loc. cit.*), but all attempts to oxidise it with selenium dioxide using different solvents have failed.

It is interesting to note that a flavone (Puddumetin, m. p. 278-80°), an isoflavone (Prunasetin, m. p. 237-38°) and a flavanone (sakuranetin, m. p. 150-52°) have been isolated from the same plant, *e.g.*, the bark of *Prunus pudum*.

EXPERIMENTAL

The substance was isolated as described by Chakravarti and Ghosh (*loc. cit.*). It forms shining, hard, almost colourless crystals, m. p. 150-52°. On high vacuum dis-

tillation it distils at 195° - 205° /0.5 mm. and at 165° /0.2 mm. It is readily soluble in cold caustic alkalis but insoluble in cold alkali carbonate and bicarbonate solutions. It gives a violet coloration with ferric chloride solution, indigo-blue coloration which rapidly changes into violet with fuming nitric acid. When reduced with magnesium powder and alcoholic hydrochloric acid in the presence of a drop of mercury, a pinkish violet coloration is produced.

The pure sample was dried over P_2O_5 in vacuum at 100 - 105° for 2 hours and was then analysed. [Found: C, 66.43; H, 4.91; OMe, 12.74. $C_{18}H_{11}O_4(OMe)$ requires C, 67.13; H, 4.89; OMe, 10.84 per cent].

Preparation of Acetyl Derivatives

(i) *Pyridine used as Condensing Agent*.—The substance (0.5 g.) was heated for 2 hours with acetic anhydride and a few drops of dry pyridine. The mixture was diluted with water and warmed on the water-bath for a few minutes. A viscous semi-solid mass separated and this on repeated treatment with ether deposited needles, m. p. 145° , sparingly soluble in ether. [Found: C, 63.87; H, 5.02; OMe, 7.70. $C_{18}H_{10}O_4(OCOCH_3)_2$ OMe requires C, 64.08; H, 4.85; OMe, 7.52 per cent].

(ii) *Concentrated Sulphuric Acid as Condensing Agent*.—The substance was heated for an hour with acetic anhydride and 2 to 3 drops of concentrated sulphuric acid. The mixture became dark in colour and was diluted with water and warmed when a turbid solution was obtained. This was extracted with ether, the ethereal extract washed, dried and ether removed when a viscous semi-solid mass separated which could not be crystallised, and on high vacuum distillation (0.2 mm.) it decomposed.

(iii) *Fused Sodium Acetate as Condensing Agent*.—The substance (1 g.) was heated for 6 to 8 hours with acetic anhydride (15 c.c.) and fused sodium acetate (5 g.). The solid obtained after treatment with water was filtered, dried and extracted with methyl alcohol. The residue which remained was crystallised from glacial acetic acid (alternatively from ethyl alcohol) as light brown crystalline powder (0.12 g.), m. p. 214 - 16° . (Found: C, 67.32; H, 4.81; OMe, 6.69 per cent). The methyl alcoholic solution on cooling deposited crystals which were filtered and dissolved in rectified spirit (charcoal) and fractionally crystallised, when two compounds were obtained: (i) colourless, well-defined crystals (0.41 g.), m. p. 144 - 45° and (ii) yellow needles (0.2 g.), m. p. 166 - 68° . [Found in (ii): C, 64.67; H, 4.81; OMe, 8.51. $C_{18}H_{10}O_4(OCOCH_3)_2$ OMe requires C, 64.86; H, 4.86; OMe, 8.38 per cent].

Deacetylation of Acetyl Compounds and Isolation of Sakuranetin

Triacetyl Compound (m. p. 144 - 45°).—The compound (0.5 g.) and 15% sulphuric acid (20 c.c.) were refluxed for 5 to 6 hours. The solution was cooled and the solid obtained extracted with 10% caustic potash solution, the alkaline solution acidified and the solid obtained was crystallised from benzene and finally from dilute alcohol as colourless needles, m. p. 150 - 51° . [Found: C, 66.88; H, 4.84; OMe, 10.90. $C_{18}H_{11}O_4(OMe)$ requires C, 67.13; H, 4.89; OMe, 10.84 per cent].

This compound gives a deep violet coloration with ferric chloride and pink coloration with magnesium powder and alcoholic hydrochloric acid.

solution was taken in the middle compartment and water in the outer ones was allowed to flow continuously at a slow rate.

During electrodialysis water in the anode compartment was found to be acidic to bromothymol blue, while that in the cathodic chamber was alkaline. At the end of the period of 70 hours, the liquids in both the chambers reached practically neutral p_H (7). The liquid in the anode chamber as well as the solution in the middle compartment were tested by $AgNO_3$ to be free from chlorine.

The waters running out from the anode and cathode chambers were separately collected, concentrated by evaporation *in vacuo*, each made up to a definite volume (250 c.c.), and tested for reducing sugars by Fehling's solution. Sugars were found to be present in both the liquids. A portion of the solution from the cathode chamber was also examined qualitatively and found to contain Ca, Mg and K. A quantitative estimation of Ca, Mg, K and the reducing sugars (as glucose) was carried out by the usual methods and expressed as percentage of the air-dried, purified specimen as presented in Table I. The solution in the middle compartment was observed to be colloidal in nature and was highly acidic. Two samples of gum jeol were treated in a similar manner (Samples 1 and 3 of Part I, this *Journal*, 1948, 25, 59). The solutions from the middle compartment are designated as sol A and sol B respectively.

An exactly similar procedure for electrodialysis was followed in the case of a gum arabic solution, previously purified by thrice precipitation with alcohol (50%), and similarly treated with HCl (0.1N). In this case it was observed that Ca, Mg and K were coming out into the cathodic chamber and Cl into the anode compartment but there was no indication for the liberation of reducing sugars into any of the outer compartments as in the case of gum jeol. Electrodialysis was continued till the central and the anode compartments were free from chlorine (Sol D). Solutions from the two outer compartments were separately collected, concentrated by evaporation at reduced pressure and each made up to a definite volume (250 c.c.). Quantitative estimations of sugar, Ca, Mg and K were carried out as before and presented in Table I.

Electrodialysis in absence of Acids.—About 100 g. of gum jeol (sample 1 of Part I) were purified by thrice precipitation with alcohol (50%) and the purified sample dried. This purified gum (20 g.) was dissolved in water and electrodialysed directly without addition of acid.

The current passing through the solution was observed in the beginning to be 0.15 amp. but in 8 hours' time it came down to 0.05 amp. only. By this time some of the gum settled down in the middle chamber which on stirring formed a uniform mixture and the current again increased to 0.1 amp. which slowly decreased with the progress of electrodialysis.

Six hours after electrodialysis was started and onwards, small quantities of liquids from the anode and cathode chambers were repeatedly tested for reducing sugars, Ca, Mg and K. Sugars were observed to come out into both the outer chambers while Ca, Mg and K were detected in the cathode chamber only. After about 65 hours the cations and sugars were found to be absent in each of the anode and cathode chambers. The

solution in the middle chamber was tested for the cations and a complete absence of these was an indication to stop further electrodialysis. A quantitative estimation of the sugars and the cations was carried out in an exactly similar manner as previously described, the results of which appear in Table I. The solution in the middle compartment has been termed Sol C.

Similar experimentation was resorted to in the case of gum arabic (purified) and the results are presented along with others in Table I (sol E).

TABLE I

Gum samples.	Conc. of added acid.	Anode compt. sugars*	Cathode compartment.			Sugars.*	Total sugars.		Complex acid.
			Ca.	Mg.	K.		Electro-dialysis.	Hydrolysis.	
Gum jeol.									
Sample 1	0.1 N	14.2%	0.8%	0.45%	0.10%	15.0%	29.2%	31%	68.7%
"	0.	15.1	0.82	0.41	0.11	15.3	30.4	—	69.0
Sample 3	0.1	15.6	0.71	0.50	0.07	14.8	30.4	29.5	71.2
Gum Arabic.									
1	0.1	0.5	0.80	0.05	0.12	0.1	0.6	—	98.7
2	0	0.2	0.82	0.03	0.15	0.3	0.5	—	98.2

* Sugars have been estimated by titration with Fehling's solution and expressed as percentage of glucose.

It will be evident from the table that the amounts of sugars coming out in the two outer compartments are almost equal and the total amount from the two compartments roughly equals that obtained by mild hydrolysis of the gum with acid (vide Part II, *loc. cit.*) in the case of gum jeol, whether acid be used during electrodialysis or not. The total amount of the bases expressed as oxide is roughly equal to the percentage of ash obtained by incineration of the purified gum (about 3%). Ca appears to be the largest in amount, while Mg comes intermediate in gum jeol, and least in gum arabic. The percentage of sugars liberated during electrodialysis of gum arabic is very small.

The acid solutions from the central compartments were then made up to 1000 c.c. in each case. Aliquot portions of these were then precipitated by alcohol, and the precipitate after washing with alcohol, and finally with alcohol-ether mixture was dried in air. The amounts of the acid recovered in this way, expressed as percentage of the purified gum, have been presented in the last column of Table I. Combustion experiments of these acid samples present the following figures (Table II).

Evidently from Table II the acids, obtained from gum jeol by electrodialysis with or without acid and also by the mild hydrolysis of the gum, as well as those obtained from gum arabic by similar methods have almost the same percentage composition. Whether the acids are of the same order of complexity (i. e., molecular weight) was tested by determination of the freezing point of a 10% solution of these which showed an approxi-

Electrodialysis of the two gums show that gum jeol is a much more complex substance than gum arabic. While gum arabic appears to be a Ca, Mg or K salt of the arabic acid, the other gum is also a mixture of the same salts of the jeolic acid but contains in addition some additional sugar molecules which remain more or less loosely bound as evident from the fact that some sugars have been found to be liberated on electrodialysis of the gum even in absence of acids. Electrodialysis of gum arabic without acid yields negligibly small quantities of sugars. Hence we conclude that gum jeol is a more complex body, being salt of jeolic acid to which some sugar molecules are further attached.

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PHYSICAL CHEMISTRY LABORATORY,
COLLEGE OF ENGINEERING AND TECHNOLOGY,
JADAVPUR, CALCUTTA.

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STUDIES ON GUM JEOL (*LANNEA GRANDIS*, SUPER). PART V.
DEPENDENCE OF VISCOUS AND ELECTROCHEMICAL
PROPERTIES OF THE AQUEOUS SOLUTION
ON ITS CONCENTRATION

BY S. N. MUKHERJEE AND (MISS) K. K. ROHATGI

Variation of physical and electrochemical properties with concentration of gum solution has been studied. Curves showing such variations with concentration all show breaks, but the regions in which these breaks appear are not identical in all cases. Gum particles can be thrown out of solution by centrifuging at a moderate speed (4000–6000 r. p. m.). These particles also have the property of taking up hydrogen ions from HCl solution, and increase its p_H when added in increasing proportions.

Gum jeol has been shown to be a mixture of Ca, Mg and K salts of a carboxylic acid to which quite a large number of sugar molecules, principally *l*-arabinose and *d*-galactose, remain attached. These sugar molecules become liberated when the gum is hydrolysed in different stages on treatment with acids (*cf.* Parts I-III of this series, this *Journal*, 1948, 25, 59, 63, 113).

Although no work on this particular gum as to its physical and electrochemical properties is recorded in the literature, previous work done on gum arabic solution presents conflicting views regarding the fundamental nature of the aqueous solution itself. One group of workers (Thomas and Murray, *J. Phys. Chem.*, 1928, 32, 677; Taft and Malm, *ibid.*, 1931, 35, 874) has inferred from their observations that these systems behave exactly as true electrolytes in aqueous solutions (*cf.* also Hammersten, *Biochem. Z.*, 1924, 144, 383). Other workers have, however, regarded this as colloidal solution having considerable electrolytic conductance (Hatschek, "Physics and Chemistry of Colloids", 1927, p. 24; Freundlich, "Colloid and Capillary Chemistry", 1922, p. 596). Kruyt and Tendeloo (*Kol.-Chem. Beih.*, 1929, 29, 396) have emphasised the lyophilic character of gum arabic from their study on the viscosity of aqueous solutions of gum arabic.

Workers belonging to the latter group are again divided amongst themselves into two sections in point of application of the classical or modern concepts of electrochemistry. Some of these hold that all the facts observed so far can be explained on the basis of Arrhenius's theory of partial dissociation (Briggs, *J. Phys. Chem.*, 1934, 38, 83; McBain, *J. Amer. Chem. Soc.*, 1928, 50, 1636; Linderström-Lang, *Compt. rend. Trav. lab. Carlsberg*, 1926, 16, No. 16). The opposite section relies upon the Debye-Hückel theory of interionic attraction for explanation of the observed facts (van Rysselberghe, *J. Phys. Chem.*, 1934, 38, 645; Pauli *et al.*, *Kolloid Z.*, 1933, 62, 162; 1937, 79, 63; "Electrochemie der Kolloide," 1929). Some again (Pauli and Valko, *loc. cit.*) are of opinion that the modern theory of interionic attraction together with the assumption of a suitable association factor would be sufficient for explaining the observed facts.

For approximately equal concentrations the data appear to be reproducible within the limits of experimental error. Repetitions of the same measurement in the same solution are also reproducible as will be evident from the concordance of the three figures in each column.

The influence of the effect of mechanical treatment on some of the physical properties was also examined. For this reason the solution was vigorously stirred in a mechanical shaker for more than an hour and the properties were measured before and after shaking. Results are shown in Table II.

TABLE II
Mechanical treatment.

Conc. of the soln. = 2.446%. Temp. = $35^{\circ} \pm 0.1$.

Properties studied.	Before shaking.	After shaking.
Relative viscosity	3.720	3.680
p_H	4.57	4.57
Sp. conductance	7.986×10^{-4}	8.017×10^{-4}

Thus the previous history of gum jeol solutions, so far as the mechanical treatment goes, has no effect on their relative viscosity, p_H and specific conductance.

DISCUSSION

Hydrogen-ion Activity.— p_H values at four different concentrations have been shown in column 2 of Table III. Hydrogen-ion activity (a_H) appears in column 3.

TABLE III

Conc. (in g. %).	p_H .	$a_H \times 10^5 N$.	a_H/c ratio.
0.49	4.398	3.990	8.0×10^{-5}
0.82	4.390	4.074	5.0
1.22	4.350	4.470	3.5
2.45	4.22	6.100	2.7

Neither p_H nor a_H appears to change very much, although the concentration change has been as much as 500%. This is very suggestive of the fact that probably the gum has an inherent buffering property. This point was further examined by the addition of increasing quantities of the gum to a fixed quantity of HCl solution and noting the changes in p_H produced. For this reason 10 c. c. of an HCl solution ($N/50$ approx.) were taken and increasing volumes of the gum solution added to it and the final volume of the mixture was made up to 20 c. c. with water. A control experiment was performed by mixing 10 c. c. of HCl solution with 10 c. c. of water. The control was observed to have a p_H of 2.3. The results of this series of experiments have been graphically represented in Fig. 1, from which it will be evident that the p_H of the HCl

solution gradually increases with addition of increasing quantities of the gum. Such large changes in the activity of H-ions cannot be wholly attributed to the changes in ionic strength of the solution brought about by increasing the concentration of the gum as envisaged in Debye-Hückel interionic attraction theory. The buffering properties of the gum can therefore be understood in the light of the H-ion reserve which it sets up as the concentration increases. These H-ions are released on dilution as will be evident from column 4 of Table III which shows the a_H/c ratio i.e., the amount of active hydrogen ions per g. of the gum increases roughly three times when the solution is diluted five times. Regarding the mechanism as to how and where these hydrogen-ions are retained by the gum molecules, the problem appears to await further experimentation.

FIG. 1

Buffering properties.

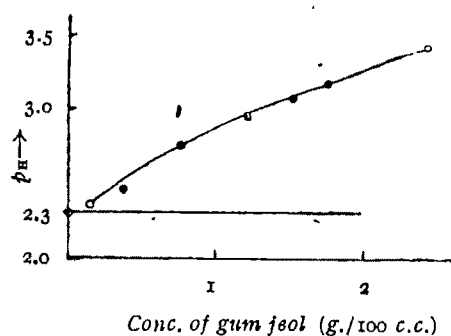
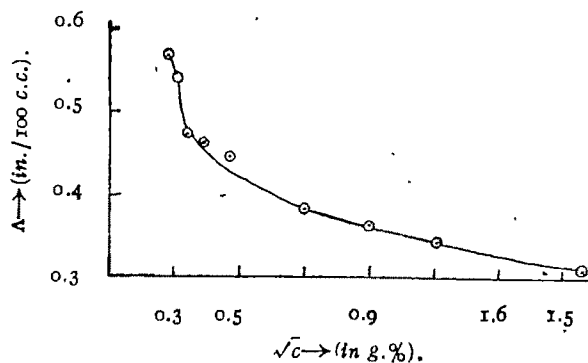


FIG. 2

 $\Lambda - \sqrt{c}$ curve.

Electrolytic Conductance.—Results of the measurements appear in Table IV. Values of specific conductance appear in row 3.

TABLE IV

*Conc.	0.079	0.094	0.116	0.153	0.224	0.489	0.855	1.223	2.446
\sqrt{c}	0.28	0.31	0.34	0.39	0.47	0.70	0.90	1.11	1.56
Sp. conduc. (R) $\times 10^4$ mho	0.448	0.509	0.552	0.710	0.992	1.882	2.971	4.209	7.595
‡Equiv. conduc (Λ)	0.570	0.542	0.476	0.464	0.447	0.385	0.365	0.344	0.311

* In g./100 c. c. sol.

‡ For 1g./100 c. c.

Since the equivalent weight of the gum is not known, the equivalent conductance in the usual sense could not be calculated. We can, however, define a quantity (Λ) which is the conductance of that volume of solution (in c. c.) which contains 1 g. of the gum, placed between two electrodes 1 cm. apart. This quantity will be strictly proportional to the actual equivalent conductance of the gum solution.

previous section, are also in agreement with the conclusion that at a concentration in the neighbourhood of 1.8 g./100 c.c., the aggregation reaches its limit and the particle size becomes maximum.

Relative Viscosity.—Results of measurements have been presented in the following table and the graphical representation in Fig. 5.

TABLE VI

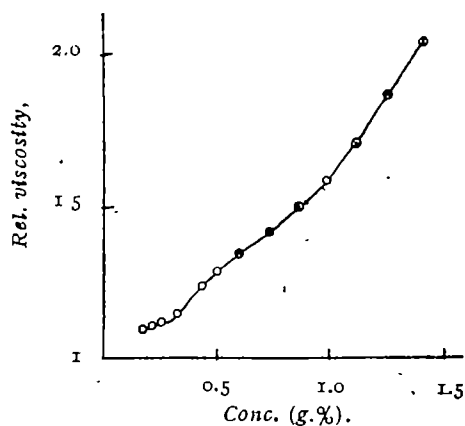
 $t = 30^\circ$.

Conc. (g./100 c.c.) ..	0.18	0.21	0.24	0.33	0.37	0.42	0.49	0.59	0.73	0.98	1.468	2.936
Rel. viscosity ...	1.089	1.090	1.123	1.132	1.160	1.227	1.272	1.338	1.406	1.569	2.038	3.869
Absolute „ (Cp) ...	0.839	0.839	0.865	0.872	0.893	0.945	0.979	1.030	1.083	1.208	1.569	2.979

The curve for gum jeol shows that the relationship is not linear. At about a concentration of 0.33 g./100 c.c. there is a break indicating a sudden increase of slope. Again at a concentration of 0.42% there is another break where the slope tends to decrease again. At higher concentrations the curve runs convex towards the concentration axis, which signifies that the viscosity increases much more rapidly than the concentration.

The mode of increase of relative viscosity at higher concentrations, as observed here, has been regarded by Kruyt and Tendeloo (*Koll.-Chem. Beih.*, 1929, 29, 396) and Taft and Malm (*loc. cit.*) as a characteristic feature of all lyophilic colloids. The behaviour exhibited by this gum stands intermediate between those of cane sugar, which is a true solution, and of gelatin, which forms a colloid. Mere analogy with a lyophilic colloid is, however, of little avail if we cannot have an insight into the mechanism which works within and which is responsible for such a rapid rise of viscosity.

To get an insight into this aspect the responsibility of hydration should be taken into consideration along with the effect of aggregation proceeding at higher concentrations. Aggregate formation with increasing concentration increases the size of the particle for which the viscosity of the solution is expected to increase. With increasing concentration again, water taken up by the micelle by way of solvation becomes considerable and the concentration of the solution becomes greater due to removal of water than what is expected from the percentage concentration. It is of course true that with increasing concentration, water available for hydration of each micelle is far less than in a dilute solution where the degree of hydration is much greater (*cf.* Hatschek,

FIG. 5
Rel. viscosity—conc. curve.

"Physics and Chemistry of Colloids," 1927). Molecules with smaller number of water molecules bound to them at higher concentrations will necessarily have smaller dimensions and will tend to decrease the viscosity; but the net effect is determined by all the simultaneously influencing factors, viz., aggregation and hydration of the micelles.

If a break in the curve signifies starting of aggregate formation, it may be concluded that the starting point is either at 0.33% or 0.42% concentration.

A study of the influence of concentration of the gum jeol solution on the properties thereof thus reveals certain peculiar features. The graphs representing the variation of such properties with concentration do not run smooth but show one or two breaks within the concentration range studied (Table VII).

TABLE VII

Nature of curves.				Concentration at	
	No. of inflexions.			1st inflexion.	2nd inflexion.
$\Lambda - \sqrt{c}$ (Fig. 2)	1	0.094%
$c \text{ v. } -c$ (Fig. 3)	2	0.28
Turbidity-conc. (Fig. 4)	2	0.50*
Relative viscosity-conc. (Fig. 5)	2	0.22

Experience gathered from centrifuging a gum solution shows that the more concentrated the solution, the less are the time and the speed at which the gum is thrown out. At higher concentrations the gum molecules therefore become bigger and heavier. Thus formation of aggregate undoubtedly proceeds with increasing concentration in the gum jeol. The concentration from which this aggregation starts is, however, not clear since different properties show inflexions in different regions and some show two inflexions (cf. the case of yeast nucleic acid, Mukherjee and Sarkar, *loc. cit.*).

Diminution of equivalent conductance with increasing concentration of gum is also quite in accordance with the observation that increasing addition of gum increases the p_H of a hydrochloric acid solution. Disappearance of H^+ -ions as more and more gum is added (Fig. 1) shows that the gum takes up the H^+ -ions which may either go to intensify the ionic atmosphere (according to Debye-Hückel interionic attraction theory) or become bound in the double layer surrounding each micelle. Mukherjee (*Kolloid Z.*, 1933, **62**, 257, *et. seq*), however, drew attention to the inadequacy of the treatment of colloidal solutions from the view point of Debye-Hückel theory or of any classical concept of electrochemistry. Although there is a certain amount of similarity, as brought out by the work of Duclaux (*J. chim. phys.*, 1907, **8**, 36; 1909, **7**, 413), Pauli (*loc. cit.*), Zsigmondy, McBain (*loc. cit.*) and others between the behaviour of colloidal electrolytes and ordinary electrolytes, there is, however, little justification for treating these two systems as exactly alike, because according to Mukherjee, the similarity observed is more apparent than real and there are essential differences which characterise the behaviour of colloidal electrolytes. He regards the colloids as a polyphase system whose electrochemical behaviours are governed by adsorption and surface energy. He suggests that

and $M/5.07$ solution of potassium ferricyanide would be referred as A/1- ferricyanide solution.

TABLE I

Strength of the solution = $M/5$

Vol. of K_3FeCy_6 soln. (v)	Alcohol added.	Time.	Obsd. titre values of $N/10-Na_2S_2O_3$ soln. for 'v' c.c. of K_3FeCy_6 soln.	Calc. titre value for 20 c.c. of K_3FeCy_6 soln.	Theo. titre value.
20 c.c.	Nil		20.05 c.c.	20.05 c.c.
18	2 c.c.	Immediate	18.05	20.06 c.c.	...
"	"	15 min.	18.05	20.06	...
"	"	30	18.05	20.06	...
"	"	1 hr.	18.05	20.06	...
16	4	Immediate	16.05	20.06	20.05
"	"	15 min.	16.05	20.06	...
"	"	30	16.05	20.06	...
"	"	1 hr.	16.05	20.06	...
"	"	Boiled	16.0	20.0	..

TABLE II

Results obtained by direct conductometric titrations

A/1- $CdSO_4$ and A/10- K_3FeCy_6 . Conc. ratio (n) = 10:1

A/10- K_3FeCy_6 in the cell (v).	Alcohol added.	$CdSO_4$ reqd. for 'v' c.c. A/10- K_3FeCy_6 in the cell (v_1).	$CdSO_4$ for 10 c.c. A/10- K_3FeCy_6 (v_1/v)10	Equiv. vol. of A/10- $CdSO_4$ $n(v_1/v)$ 10	Curve No.
10 c.c.	0.0 c.c.	1.37 c.c.	1.37 c.c.	13.7 c.c.	1
9	1.0	1.22	1.36	13.6	2
8	2.0	1.07	1.34	13.4	3

A/2- $CdSO_4$ and A/10- K_3FeCy_6 . Conc. ratio (n) = 5:1

10 c.c.	0.0 c.c.	2.76 c.c.	2.76 c.c.	13.80 c.c.	4
9	1.0	2.46	2.73	13.65	5
8	2.0	2.16	2.70	13.50	6

TABLE III

*Results obtained by reverse conductometric titrations.*A/2-K₃FeCy₆ and A/10-CdSO₄. Conc. ratio (n)=5:1

A/10-CdSO ₄ in the cell (v).	Alcohol added.	K ₃ FeCy ₆ reqd. for CdSO ₄ in the cell (v ₁).	K ₃ FeCy ₆ calc. for 10 c.c. A/10-CdSO ₄ (v ₁ /v) ₁₀	Equiv. vol. of A/10- K ₃ FeCy ₆ n(v ₁ /v) ₁₀ .	Curve No.
10 c.c.	0.0 c.c.	1.35 c.c.	1.35 c.c.	6.75 c.c.	7
9.0	1.0	1.24	1.38	6.90	8
8.0	2.0	1.16	1.45	7.25	9

A/4-K₃FeCy₆ and A/10-CdSO₄. Conc. ratio (n)=2.5:1

10.0 c.c.	0.0 c.c.	2.74 c.c.	2.74 c.c.	6.85 c.c.	10
9.0	1.0	2.50	2.78	6.95	11
8.0	2.0	2.32	2.90	7.25	12

DISCUSSION

In continuation of our previous studies on the composition of copper and cadmium ferrocyanides (*J. Indian Chem. Soc.*, 1947, **24**, 487, 499; 1948, **25**, 27, 185, 191, 220) we observe that the composition of cadmium ferricyanide leads to more interesting observations as the composition is of a different order than those of copper and cadmium ferrocyanides. From the strengths of the solutions of cadmium sulphate (*M*/4.82) and potassium ferricyanide (*M*/5.07), the theoretical titre values for 10 c.c. of potassium ferricyanide solution for the formation of the compounds KCdFeCy₆, Cd₃(FeCy₆)₂ and KCd₁₀(FeCy₆)₇ in direct titrations are 9.5, 14.25 and 13.5 c.c. respectively of the cadmium sulphate solution. The theoretical titre values for 10 c.c. of cadmium sulphate solution for the formation of the same compounds in the reverse titrations are respectively 10.52, 7.01 and 7.37 c.c. of ferricyanide solution.

The observed titre values in the direct and reverse titrations can be said to approximate the theoretical titre values for the formation of the compounds Cd₃(FeCy₆)₂ and KCd₁₀(FeCy₆)₇. The possibility of the formation of the compound KCdFeCy₆ is ruled out on the basis of the conductometric results.

The observed titre values for 10 c.c. of potassium ferricyanide solution in aqueous medium is 13.7 to 13.8 c.c. of cadmium sulphate solution. In presence of increasing amounts of alcohol the observed titre values decrease, and almost approach the theoretical titre value for the formation of the compound KCd₁₀(FeCy₆)₇. In view of the influence of hydrolysis upon such complexes (*loc. cit.*) it is expected that the observed titre values in the direct titrations in aqueous medium would be higher than the theoretical titre values, because the ferricyanide, released as a result of the hydrolysis, would consume some amount of cadmium sulphate solution. In presence of increasing

the theoretical titre values are due to slightly greater adsorption of Cd^{++} ions by the precipitated complex than the $(\text{FeCy}_6)^{+++}$ ions.

Experiments on hydrolysis, and of adsorption of Cd^{++} and $(\text{FeCy}_6)^{+++}$ ions by cadmium ferricyanide sol are in progress and will be communicated in a subsequent communication.

Thus, on the basis of the conductometric study, it can be concluded that cadmium ferricyanide corresponds to $\text{KCd}_{10}(\text{FeCy}_6)_7$, and it is stabler than the corresponding ferrocyanide (Parts IV, V and VI).

Thanks of the authors are due to Dr. S. S. Deshapande, Head of the Chemistry Department, Agra College, for his kind interest in the progress of these investigations and also to Dr. K. C. Mehta, the Principal, Agra College for the extension of the Research fellowship granted to one of us (H. C. G.).

CHEMICAL LABORATORIES,
AGRA COLLEGE, AGRA.

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STUDIES IN BACTERIAL AMYLASES. PART II. THE SOURCE OF CARBON AS A DETERMINANT IN AMYLASE FORMATION BY *B. SUBTILIS*

BY BHAGWAN S. LULLA

The effect of different polysaccharides, sugars, sugar alcohols and salts of lactic acid, as sources of carbon have been studied. Starch yields the highest amount of the amylases, next in order come sucrose, dextrin, fructose, arabinose, glucose, mannose, maltose, mannitol, lactose, xylose, pectin, dulcitol and rhamninose. Galactose, raffinose and inulin were found to be poor enzyme formers. Lactates do not form a good source of carbon.

During the studies on the nutritional requirements of diastase producing bacteria, it was found of great interest to investigate the suitable sources of nitrogen and carbon, playing a very important role in the formation of amylase. The work on the suitability of the various forms of nitrogen has already been described in the previous communication (Lulla, this *Journal*, 1948, 25, 119). The present work therefore deals with the effect of different sources of carbon in relation to amylase formation in bacteria (*B. subtilis*, N. C. T. C., 2027 N). Brunton and Macfadyan (*Proc. Roy. Soc.*, 1889, 46, B, 542) reported that amylase was produced in the case of two bacteria only when grown on starch and not on meat extract. Dox (*Bur. Animal Ind.*, Bull. No. 120, U. S. Dept., Agrl., 1910) postulated that the amount of carbohydrase elaborated could be materially increased by cultivating the organism on a particular substratum. This was found to be particularly true in the case of amylase, lactase and inulase, enzymes of fungal origin. Biodin and Effront (U. S. Patent 1,227,374; May 22, 1917) employed the starch or enzymatically digested starchy materials as a source of carbon for the growth of *B. subtilis* and *B. Mesentericus* in relation to amylase formation. The studies have also been conducted with the extracts of different naturally occurring materials, rich in carbohydrates by various workers (Tilden and Hudson, *J. Amer. Chem. Soc.*, 1942, 64, 2139, 1432; Beckord, Kneen and Lewis, *Ind. Eng. Chem.*, 1945, 37, 692) during their investigations on the amylase formation with different organisms. No where in the literature, comparative data regarding the efficiency of the different carbon sources employed for the cultivation of the diastase producing bacteria, using one single strain, has been observed. The present studies have therefore been made to find out the effect of the various sources of carbon on the formation of amylase. Among the various sources of carbon tried, the following classes of compounds have received attention.

1. Carbohydrates which includes: (a) Pentoses (arabinose and xylose); (b) Hexoses (glucose, mannose, fructose and galactose); (c) Disaccharides and trisaccharides (sucrose, maltose, lactose, rhamninose and raffinose); (d) Polysaccharides (starch, dextrin, inulin and pectin); (e) Sugar alcohols (mannitol and dulcitol).

2. Lactates of sodium, potassium and calcium.

EXPERIMENTAL

During these studies the media of the following composition were employed in order to find out the effect of different sources of carbon on the formation of bacterial amylase,

Media composition.—Culture medium (10 ml.), previously adjusted to p_H 7.0, consisted of 1.0 ml. of basal medium (Lulla, *loc. cit.*), 1.0 ml. of ammonium lactate solution equivalent to 2.0 mg. level of nitrogen which served as a nitrogen source, and the carbon source which was variant during these investigations was added so as to give the final ratio of nitrogen to carbon as 1:13.

FIG. 1

Effect of starch and its hydrolytic compounds on the formation of amylase.

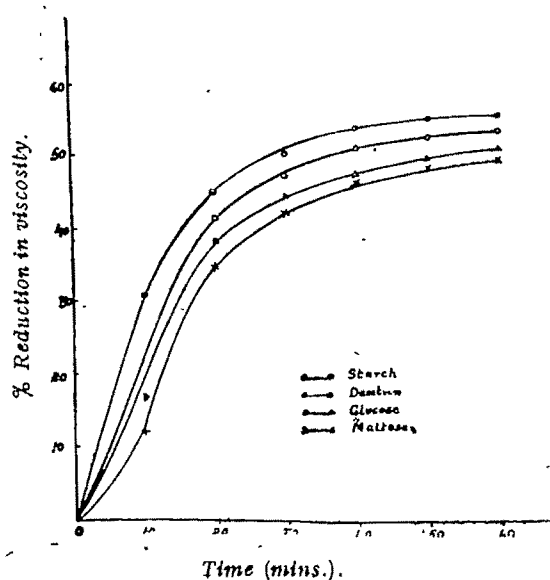


FIG. 2

Effect of diff. sugars on the formation of amylase

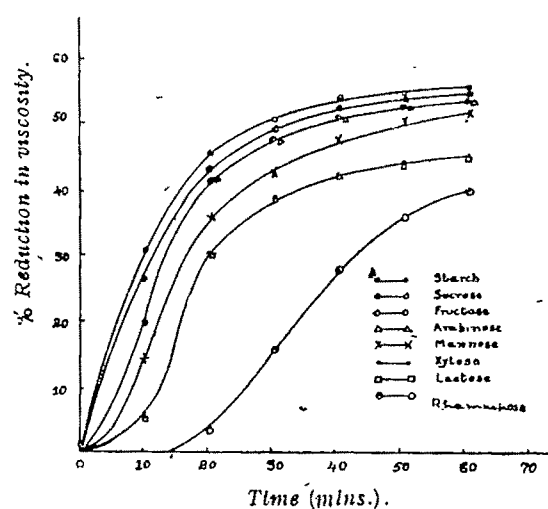
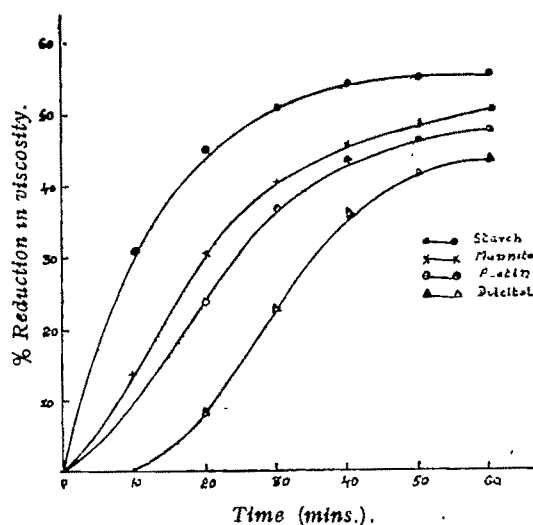


FIG. 3

Effect of polysaccharides and sugar alcohols on the formation of amylase



The methods of growing the bacteria and assaying the amylase activity have been described previously (Lulla, *loc. cit.*). The results obtained with various carbon sources are represented in the Figs. 1-3 and the units of amylase calculated per 10 ml. of the culture medium are also expressed in Table I.

TABLE I

Polysaccharides		Oligo saccharides		Monosaccharides	
Source of carbon.	*Enzyme unit.	Source of carbon.	*Enzyme unit.	Source of carbon.	*Enzyme unit.
Starch	112.5	Maltose	60.0	Glucose	69.2
Dextrin	80.0	Sucrose	94.7	Mannose	64.2
Inulin	Negligible	Lactose	50.0	Galactose	Negligible
Pectin	42.4	Raffinose	Negligible	Fructose	80.0
		Rhamninose	24.8	Arabinose	80.0
Lactates of				Xylose	47.4
sodium	Negligible				
potassium	Do			Sugar alcohol	
calcium	Do			Dulcitol	29.6
				Mannitol	51.4

*per 10 ml. of culture medium

DISCUSSION

Two sources of carbon which have been investigated fall into two broad groups:—

- The carbohydrates, which include a variety of pentoses, hexoses, di- and tri-saccharides, sugar alcohols and a few typical polysaccharides.
- The lactates of sodium, potassium and calcium.

So far as carbohydrate series is concerned, the most luxurient growth of the bacteria and the highest yield of the enzyme are secured by providing starch as the source of carbon; on the other hand, the negligible quantity of the enzyme is formed when galactose, raffinose and inulin are respectively furnished as a source of carbon. The bacteria was seen to thrive with equal facility on most of the carbohydrates tried as on starch, but its efficiency regarding enzyme formation varied with the individual source of carbohydrate.

The lactates were tried because of the previous finding (Lulla, *loc. cit.*), that ammonium lactate furnished the best source of nitrogen, in the culture media. It was therefore suggested that lactate must constitute a very easily assimilable source of carbon. This expectation has not been realised as negligible quantity of the amylase is formed in case of lactates other than ammonium lactate. It must now be accepted that it is only as the ammonium salt that it exerts a very favourable effect on the formation of amylase.

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ERRATA

In part I of this series published in the March issue of this journal. *Read*

in page	in line	1917	for	1937
119	31			
121	8	in Table II	„	in Table I
„	12 (Table I)	10	„	10
126	11	amylase	„	amylase

EFFECT OF SNAKE VENOMS ON THE OXIDATION OF GLUCOSE AND ITS METABOLITES IN CELL SUSPENSIONS

By B. N. GHOSH AND A. K. CHATTERJEE

The effect of the venoms of a number of snakes, on the oxidation of glucose, lactic, pyruvic and succinic acids by pigeon brain suspension in the presence of air, has been investigated. It has been found that the oxidation of these substrates are inhibited to the extent of 82 to 90% by the venoms at as low a concentration as 0.033 mg./c. c. The effect of cobra venom on the anaerobic oxidation of glucose and succinic acid has also been investigated using Quastel's ferricyanide technique. These results show that cobra venom at a concentration of 0.033 mg./c. c. affects the succinic dehydrogenase only to a small extent. It has therefore been inferred that this venom even at low concentrations can strongly inhibit the activity of the cytochrome-cytochrome oxidase system.

It has been reported by Chain (*Quart. J. Exp. Physiol.*, 1937, **26**, 299 ; 1938, **27**, 49) that venoms of a number of snakes, when added in suitable doses, can strongly inhibit glycolysis in systems containing cell-free muscle extracts and fermentation in yeast maceration juice. He further states that the antifermenting principle of a venom can be neutralised by the corresponding antivenin. The effect of black tiger snake venom on a number of oxidases and dehydrogenases has also been investigated by him (*Biochem. J.*, 1939; **33**, 407). From the results Chain concludes that only those dehydrogenases, which require a co-enzyme for their activation, are completely inhibited, while the others are affected either slightly or not at all. In this connection, experimental data have been recorded showing that co-enzyme I is destroyed, when it is incubated with black tiger snake venom for $1\frac{1}{2}$ hours at 37°.

In view of the interesting observations mentioned above, it is worth investigating the effect of the venoms of some of the common species of poisonous snakes of India on the oxidation of glucose and its metabolites by tissue suspensions. The experiments of Chain (*loc. cit.*) and of Chain and Goldsworthy (*Quart. J. Exp. Physiol.*, 1938, **27**, 375) have been carried out using cell-free extracts of muscles or enzyme preparation in which the tissues have been ground with sand and buffer solution, the fluid strained through muslin and finally centrifuged. In our experiments, suspensions of pigeon brain cells have been used as the source of the enzyme. This choice has been made in view of the fact, that the brain contains the most important nerve centres and some of the venoms used by us have got a paralysing effect on the nervous system. The results obtained differ in certain important respects from those obtained by Chain (*loc. cit.*). It has been observed by us that the oxidation of succinic acid, lactic acid and pyruvic acid and glucose are to the same extent inhibited by cobra venom at a low concentration. The oxidation of the substrates mentioned above is inhibited by about 90% by even 0.033 mg. of cobra venom per c.c. Since succinic dehydrogenase does not require a co-enzyme for its activation, the observed inhibition cannot be accounted for on the basis of the destruction of co-enzyme I. The alternatives which suggest themselves are that either the dehydrogenases involved in these reactions are affected or that the cytochrome-cytochrome oxidase system, which takes part in all these reactions, is inhibited by cobra venom. From the data recorded in this paper, the cytochrome-cytochrome oxidase system appears to be affected.

E X P E R I M E N T A L

Estimation of the Toxicity of the Venoms.—The venoms of cobra, banded krait and Russell's viper were used in these experiments. Fresh solutions, in physiological saline containing known weights of dry venom, were prepared shortly before use. Pigeons weighing between 300 and 310 g. were selected as experimental animals. The minimum lethal doses were determined in the cases of cobra and banded krait venoms by intramuscular injections and in the case of Russell's viper venom by intravenous injection. By these methods, the minimum lethal doses have been found to be 0.1 mg. and 1.5 mg. for cobra and banded krait venoms respectively and 0.01 mg. for Russell's viper venom.

Preparation of the Tissue.—The cerebrum and the cerebellum were taken out of the head of the pigeon immediately after its decapitation. The material was dried by pressing lightly with filter papers, cooled in a frigidare for a few minutes, and then minced into a fine pasty mass.

Composition of the Medium.—The medium, in which the brain cells were suspended, consisted of phosphate-Ringer solution of p_H 7.3, prepared according to Peters *et al.* (*Biochem. J.*, 1933, **27**, 842). The Ringer solution had the composition: NaCl, 0.9%; KCl, 0.025%; $CaCl_2$, 0.03% and $NaHCO_3$, 0.015%. To 786 c.c. of the Ringer solution 200 c.c. of 6.8% KH_2PO_4 solution were added and then 13.9 c.c. of 20% of NaOH solution to bring the p_H to 7.3. After allowing to stand for one day, the precipitate was removed by filtration.

Measurement of Oxygen Uptake.—The oxygen uptake was measured in the Warburg manometers at $37.5^\circ \pm 0.1$. The finely chopped brain (100 mg. portion) was placed into each of a number of Warburg flasks, broken up with a thin glass rod and suspended in the phosphate-Ringer solution of p_H 7.3. The desired amount of the venom, dissolved in phosphate-Ringer, was added to the brain where necessary. The substrate solution (0.2 c.c.) in phosphate-Ringer was kept in the side-tube of each flask, while 0.2 c.c. of phosphate-Ringer only was kept in the side-tubes of the controls. 20% KOH solution (0.2 c.c.) and a small roll of filter paper were carefully introduced into the inner cup of each. The total volume of the liquid in each flask was made up to 3.0 c.c. The flasks were attached to the manometers and finally shaken in a thermostat at $37.5^\circ \pm 0.1$ for a period of $1\frac{1}{2}$ hours, the system being filled with air. By this procedure much of the substrates in the brain cells was oxidised and the venom also exerted its full effect on the cells. After this period of shaking, the substrate was tipped off into the reaction mixture contained in the flasks, the level of the manometric fluid adjusted, and the stop-cocks of the manometers were closed. The oxygen uptake was measured at intervals of 15 minutes for a period of one hour. The results are expressed in terms of cubic millimeters of oxygen absorbed per hour by one gram of the moist tissue.

The data recorded in Table I show the effect of the venoms of cobra, banded krait and Russell's viper on the oxidation of glucose, while those in Table II show the effect of cobra venom alone on the oxidation of succinic, lactic and pyruvic acids in the presence of the pigeon brain cells.

TABLE I

The effect of different snake venoms on the oxidation of glucose

Conc. of glucose in each case = 0.2%.

No. of expt.	Venom (mg./c c of suspension).	Cu. mm. of oxygen absorbed per g./hr. by				% Inhibition	
		Brain.	Brain+ substrate	Brain+ substrate+ venom.	Brain+ venom.	Obs.	Mean.
Cobra.							
1	0.33	564	1100	204	160	90	91
2	"	234	756	129	74	89	
3	"	625	1042	190	161	93	
4	0.17	500	993	189	140	90	89
5	"	671	806	168	149	86	
6	"	705	1190	237	198	92	
7	0.033	492	905	123	87	88	87
8	"	559	1054	221	149	86	
9	"	369	856	145	87	88	
B. krait.							
10	0.033	480	840	166	130	90	86
11	"	520	950	233	160	83	
12	"	560	980	213	150	85	
13	0.0033	560	870	190	140	84	81
14	"	428	798	192	111	78	
15	"	340	762	170	92	82	
Russell's viper.							
16	0.033	530	780	120	90	88	89
17	"	470	780	115	84	90	
18	"	450	756	113	82	90	
19	0.0033	440	660	150	120	90	88
20	"	510	815	171	125	85	
21	"	425	835	159	110	88	

TABLE II

The effect of cobra venom on the oxidation of the sodium salts of the organic acids

Conc. of the substrate = 0.033M in each case.

No. of expt.	Substrate used.	Venom (mg./c.c. of suspension).	Cu. mm. of oxygen absorbed per g./hr. by				% Inhibition	
			Brain.	Brain + substrate.	Brain + venom.	Brain + venom + substrate.	Obs.	Mean.
1	Sodium succinate	0.033	369	1166	87	200	85	89
2		"	420	1240	110	192	90	
3		"	262	1081	72	138	92	
4	Sodium lactate	0.067	439	1240	74	295	72	71
5		"	443	1079	181	372	70	
6		0.170	362	681	81	113	90	
7		"	470	790	121	137	95	93
8		"	292	600	70	85	95	

TABLE II (contd.)

No. of expt.	Substrate used.	Venom (mg./c. c. of suspension).	Cu. mm. of oxygen absorbed per g./hr. by				% Inhibition	
			Brain.	Brain + substrate.	Brain + venom.	Brain + venom + substrate.	Obs.	Mean.
9	Sodium lactate	0.033	380	700	92	130	88	
10		"	420	680	108	134	90	90
11		"	290	672	82	113	92	
12	Sodium pyruvate	0.330	344	744	87	103	96	
13		"	443	604	186	206	92	93
14		"	320	781	62	103	91	
15		0.170	406	1116	136	258	83	
16		"	406	1153	161	282	84	83
17		"	418	1090	149	271	82	
18		0.033	382	986	191	330	77	
19		"	420	1010	180	269	85	82
20		"	240	760	92	170	85	

From the data in Table I the oxidation of glucose appears to be strongly inhibited by the venoms of cobra, banded krait and Russell's viper. The data in Table II show that the oxidation of the succinic, lactic and pyruvic acids are also inhibited very strongly by cobra venom. These oxidations have been carried out in the presence of air. It is therefore worth investigating the action of cobra venom on the oxidation of some of these substrates under anaerobic conditions using Quastel's ferricyanide technique (*Biochem. J.*, 1938, **32**, 936).

Effect of Cobra Venom on the Anaerobic Oxidation of Glucose and Succinic Acid.—The principle underlying this method is that in presence of ferricyanide and bicarbonate, the hydrogen of the substrate molecule reduces one mole of ferricyanide and forms thereby one hydrogen ion, which then liberates one mole of CO_2 from the bicarbonate. Thus for each mole of ferricyanide reduced, one mole of CO_2 is evolved and this can be measured manometrically.

Approximately 100 mg. of finely minced brain tissue of the pigeon were weighed out in separate Warburg flasks and broken up in a Ringer bicarbonate solution of the following composition: NaCl , 0.15 *M*; KCl , 0.006 *M*; CaCl_2 , 0.001 *M* and NaHCO_3 , 0.025 *M*; 0.2 c.c. of a ferricyanide-bicarbonate solution, prepared by mixing 5 c.c. of 10% K_3FeCy_6 with 1 c.c. of 0.16 *M*- NaHCO_3 solution. In the case of glucose, 0.1 c.c. of an 1% methylene blue solution was also added to the brain suspension. 0.6% Glucose (1 c.c.) or 1 c.c. of 0.1 *M*-sodium succinate in bicarbonate-Ringer was kept in the side-tubes of some of the flasks. The venom, dissolved in bicarbonate Ringer, was added to the brain suspension in a suitable dose. Necessary controls were kept. The flasks were attached to the manometers and the air displaced by a mixture of 95% N_2 and 5% CO_2 . To ensure perfect anaerobiosis, sticks of yellow phosphorus were kept in the inner cup of each flask. The flasks were shaken in a thermostat at $37.5^\circ \pm 0.1$ for $\frac{1}{2}$ hour and then the substrates from the side-tubes were dropped into

the main compartment. The level of the liquid in the manometers was adjusted and the CO_2 evolution was measured for 1 hour at intervals of 15 minutes. The results are recorded in Table III.

TABLE III

The effect of cobra venom on the anaerobic oxidation of glucose and succinic acid

The CO_2 evolution was measured after $1\frac{1}{2}$ hours' incubation with venom.

No. of expt.	Substrate used.	Venom used (mg./c. c. of brain suspension).	Cu. mm. of CO_2 evolved per g./hr. by				% Inhibition	
			Brain.	Brain + substrate.	Brain + venom.	Brain + venom.	Obs.	Mean.
1	Sodium succinate	0.033	240	1580	1250	340	32	
2		"	210	1100	910	260	28	29
3		"	260	1620	1340	340	27	
4	Glucose	0.0033	250	1400	1560	310	—	—
5		"	160	910	1240	230	—	—
6		0.033	710	960	320	310	95	
7		"	650	930	310	300	96	96

It is evident from the data recorded in Table III that under anaerobic condition, the oxidation of glucose is inhibited to the extent of 96% by cobra venom at a concentration of 0.033 mg./c. c. In the case of succinic acid, however, the same concentration of the venom produces an inhibition of only about 29%. This shows that cobra venom affects succinic dehydrogenase only to a small extent.

DISCUSSION

An examination of the data recorded in the paper brings out the following facts.

The oxidation of glucose is inhibited to the extent of 86 to 89% by the venoms of cobra, banded krait and Russell's viper at a concentration of 0.033 mg./per c. c. Increase or decrease of concentration of the venoms by ten times of this value raises or lowers the inhibition only slightly, thereby indicating that the maximum effect the venoms can produce is practically reached at as low a concentration as 0.0033 mg.

Similarly cobra venom can also inhibit the oxidation of succinic, lactic and pyruvic acids to the extent of 82 to 90% at a concentration of 0.033 mg./c. c. The same concentration of cobra venom (*e.g.*, 0.033 mg./c. c.) thus brings about the same degree of inhibition, 82 to 90% in the case of glucose, lactic, pyruvic and succinic acids, although the first three of the substrates require a co-enzyme and the last one does not require any co-enzyme for the purpose of oxidation. This fact leads to the conclusion that of the various mediators involved in the process of transfer of hydrogen and its final oxidation by molecular oxygen, a particular one, which participates equally effectively in the oxidation of each of these substrates, is affected by cobra venom. It is well known that in the final stage of oxidation by molecular oxygen, the cytochrome-cytochrome oxidase system is involved. Cobra venom therefore seems to affect the cytochrome-cytochrome.

oxidase system, thus bringing about the inhibition. This inference is further borne out by the fact that this venom affects succinic dehydrogenase only to a small extent which is quite insufficient to account for the total inhibition of 82 to 90% observed by us. It is to be clearly understood, however, that the possibility of the existence of a phosphatase in cobra venom, which can hydrolyse co-enzyme I, has not been denied by us. The point that we like to emphasise here, is that under the condition of our experiments, the cytochrome-cytochrome oxidase system is also affected by cobra venom and this alone can fully account for the observed inhibition.

C O N C L U S I O N

The oxidation of glucose by suspension of pigeon brain cells is strongly inhibited by the venoms of the cobra, banded krait and Russell's viper even at a low concentration.

Cobra venom has also a marked inhibiting effect on the oxidation of lactic, pyruvic and succinic acids by suspensions of pigeon brain cells in the presence of air.

The oxidation of succinic acid in presence of ferricyanide in an anaerobic atmosphere is affected by cobra venom only to a small extent. Under similar conditions, however, the oxidation of glucose is very strongly affected.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE AND
TECHNOLOGY, CALCUTTA.

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STEROID COMPOUNDS. PART II. ON A ROUTE TO THE SYNTHESIS
OF STEREOCHEMICALLY HOMOGENEOUS STEROID
KETONES*

BY PRATUL CHANDRA MUKHARJI

Addition of HCN to the $\alpha\beta$ -double bond of Hagemann's ester, followed by alcoholysis, reduction and hydrolysis affords exclusively *trans*-1-methylcyclohexane-1:2-dicarboxylic acid. The exclusive formation of the "*trans*" isomer suggests that the addition to the double bond pursues a single course. The reactions have been extended to the dicyclic analogue of Hagemann's ester, where the products also appear to be stereochemically homogeneous. The possibility of the application of this method for the synthesis of steroid ketones with "*trans*" fusion of the rings B/C and C/D has been pointed out.

In Part I of this series (Mukharji, *J. Indian Chem. Soc.*, 1947, **24**, 91), a method for the synthesis of steroid skeleton with the two angular methyl groups has been described. This method, although useful for the construction of skeletons corresponding to the formula of the natural steroid compounds, as they are written on the paper, is not, however, in the least suitable for the ultimate total synthesis of the compounds of this group. On account of the presence of a large number of asymmetric centres in the steroid molecule, and consequently the possibility of the existence of a large number of isomers, which are structurally the same but stereochemically different, the synthetic approach in this field is a very formidable task. This aspect of the problem has been discussed by Robinson in the following language in a very recent publication (Cornforth and Robinson, *Nature*, 1947, **160**, 737) "...The outcome has been that the structures of the chief members of the rapidly expanding family of substances are known in so far as that is possible without the final confirmation of successful synthesis. The latter task has been regarded as one of the most difficult that can be undertaken by the organic chemist for the simple reason that it is far from sufficient to devise a method of constructing a substance corresponding to the formula as written on the paper, difficult though that may be in itself. The molecule of dihydrocholesterol contains 9 asymmetric carbon atoms and hence 512 stereoisomers are possible. There is reason to believe that all these should be capable of existence. Even if the side-chain is not present and the position C₁₇ (steroid numbering) carries a carbonyl group there are still 128 stereoisomeric forms".

It is thus evident that unless suitable precautions are taken to prevent the formation of isomers at the intermediate stages of synthesis, the final product will invariably contain a mixture of a large number of stereoisomers. The isolation of the individuals from such a mixture involving the tedious process of fractional crystallisation is no doubt a very difficult task, which may not even succeed to the desired extent if the number of isomers in the mixture is large. And finally, although the separation of the individual isomers may be achieved, a definite characterisation of the stereoisomers still remains a very complicated problem.

* A preliminary note was published in the *Science & Culture*, 1947 **13**, 39.

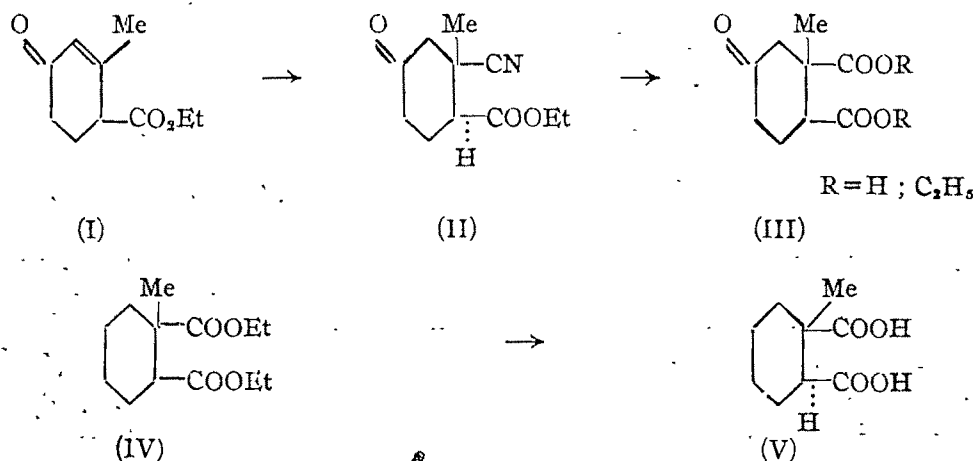
In all the known steroids the rings B/C and C/D are fused in the *trans* position ; variations occur only in respect of the fusion of the rings A and B, which are fused in the *cis* position (Coprosterol, bile acids) or in the *trans* position (dihydrocholesterol, androsterone) in various derivatives.

A new synthetic route has now been investigated in a number of preliminary experiments and this route possesses the important feature, that not only can the stereochemical vagaries be placed under the maximum control, but the products may possibly consist almost completely, if not wholly, of only one single stereoisomer, the stereochemical nature of which can be ascertained to a fair extent from the method of its formation. The preliminary experiments, so far carried out with simpler systems, show that the reactions that will be employed in the actual synthesis of the steroid ketones, rather remarkably lead to stereochemically homogeneous intermediates which belong to the stereochemical series of the desired type. From such intermediates the synthesis of the tetracyclic systems will follow conventional route, which has been pointed out later on.

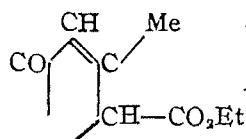
Ethyl 4-keto-2-methyl- $\Delta^{2:3}$ -cyclohexen-1-carboxylate, Hagemann's ester (I) (Hagemann, *Ber.*, 1893, 26, 876; Rouault and Smith, *J. Amer. Chem. Soc.*, 1943, 65, 631) smoothly adds up the elements of hydrocyanic acid to the $\alpha\beta$ -double bond (cf. Lapworth, *J. Chem. Soc.*, 1906, 89, 950) to yield the nitrile (II), which has been converted into the corresponding keto-diester (III, R=Et) by treatment with alcoholic hydrogen-chloride (cf. Pfeiffer and Matton, *Ber.*, 1911, 44, 1113). Considerable difficulty has been encountered in all attempts for the direct conversion of the keto-nitrile (II) into the corresponding keto-diacid (III, R=H); treatment with concentrated hydrochloric acid or with a mixture of concentrated sulphuric acid and acetic acid under a variety of experimental conditions proved futile. The keto-diester (III, R=Et) has been reduced with amalgamated zinc and alcoholic hydrogen chloride (cf. Schneider and Spielman, *J. Biol. Chem.*, 1942, 142, 351), and the resulting diester (IV) on hydrolysis with concentrated hydrochloric acid furnishes *trans*-1-methylcyclohexane-1:2-dicarboxylic acid (V) (Linstead and Millidge, *J. Chem. Soc.*, 1936, 478; Bachmann and Kushner, *J. Amer. Chem. Soc.*, 1943, 65, 1963), which is also obtained directly when the above keto-diester (III, R=Et) is reduced with amalgamated zinc and concentrated hydrochloric acid according to conventional Clemmensen procedure. The melting point of the above dicarboxylic acid (V) is not depressed when mixed with an authentic specimen of *trans*-1-methylcyclohexane-1:2-dicarboxylic acid.* It is of considerable interest to note here that in this synthesis only the *trans* isomeride of the acid is formed exclusively; the simultaneous formation of some *cis* form of the acid has not been observed so far. The homogeneous nature of the dicarboxylic acid (V), thus obtained, suggests that the addition of HCN to the $\alpha\beta$ -double bond (I) proceeds in an uniform manner to yield the nitrile (II) where the CN and the CO₂Et groups are also placed obviously in the *trans* position. The preferential and almost exclusive formation of the *trans* isomer in this synthesis is probably to be attributed to the steric influence of the carbethoxyl group in (I) and also perhaps to the repulsive action between this carbethoxyl group and the incoming cyano group, both of which are negative in character. It may be mentioned here that in all previous syn-

* Kindly supplied by Prof. W. E. Bachmann.

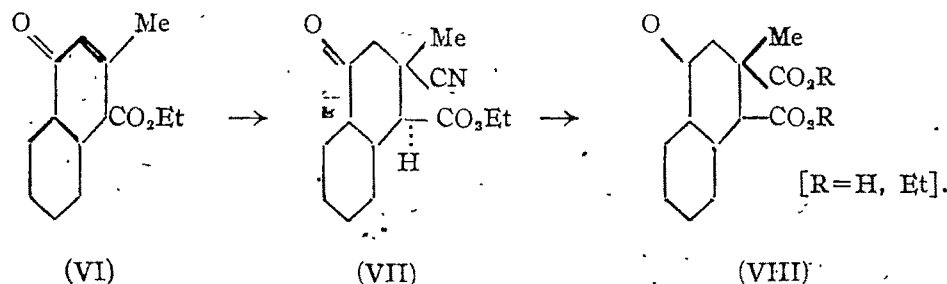
theses of 1-methylcyclohexane-1:2-dicarboxylic acid (Linstead and Millidge, *loc. cit.* Bachmann and Kushner, *loc. cit.*) a mixture of the *cis* and the *trans* isomers has invariably been obtained, which are separated by repeated crystallisation.

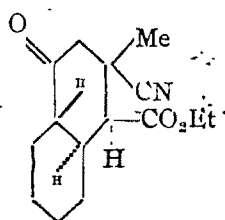


In an analogous manner, the dicyclic analogue of Hagemann's ester, ethyl *trans*-4-keto-2-methyl- $\Delta^{2:3}$ -octahydronaphthalene-1-carboxylate (VI, Barret, Cook and Linstead, *J. Chem. Soc.*, 1935, 1066) smoothly adds up HCN to the $\alpha\beta$ -double bond to yield the keto-nitrile (VII). This has been obtained as colourless silky needles, m. p. 116° - 17° , and appears to be stereocchemically pure. Treatment with alcoholic hydrogen chloride furnishes the corresponding keto-diester (VIII, R = Et) as a highly viscous liquid. Now, the probable factors which govern the course of addition of HCN to the $\alpha\beta$ -double bond are identical in both the cases (I and VI), because the relative disposition of the grouping

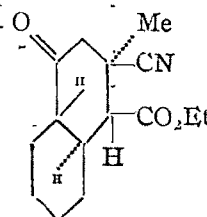


is the same in each case. It may reasonably be concluded therefore that the CN and the CO_2Et groups in the dicyclic compound (VII) are also placed in the *trans* position, as has been proved to be the case in the monocyclic derivative (II).





(IX)

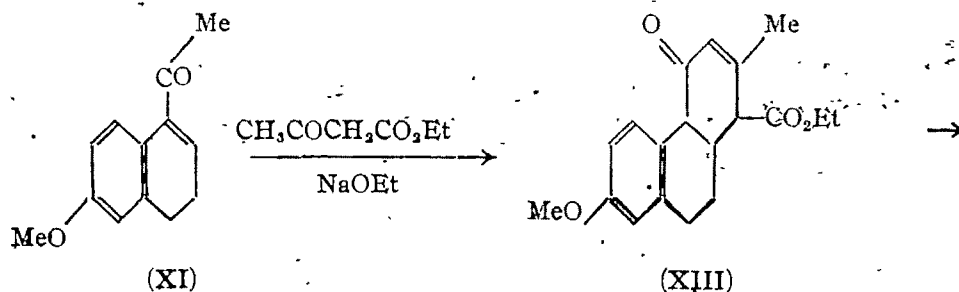


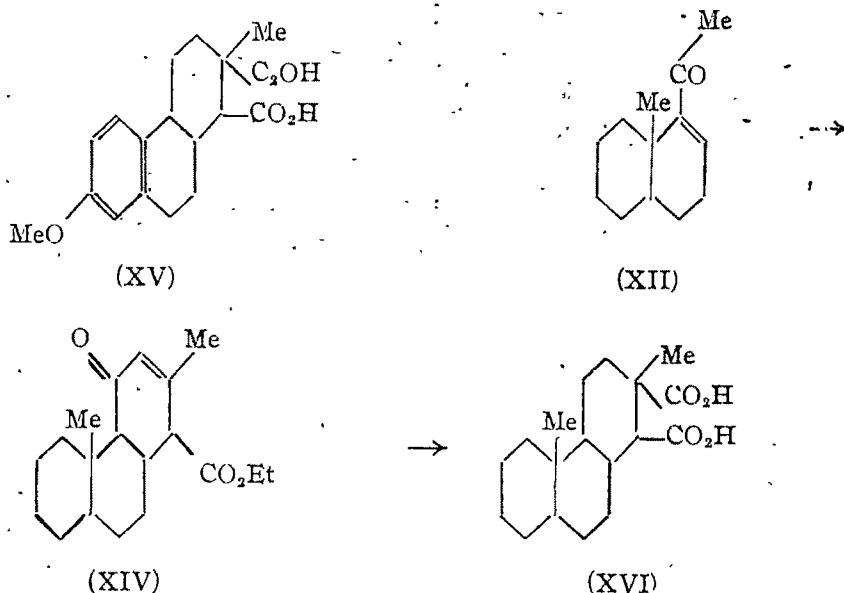
(X)

Now, even accepting that the two rings and the CN and CO₂Et groups in the dicyclic keto-nitrile (VII) occur in the *trans* configuration, two isomerides of the compound (VII) are still possible depending upon the orientation of the methyl group and one of the angular hydrogen atoms as represented in figures (IX) and (X). In view of this possibility, the keto-nitrile (VII) has been subjected to careful fractional crystallisation. So far the product appears to be quite homogeneous, only the one particular form (m. p. 116°-117°) mentioned earlier has been obtained. It is quite likely that the other possible form is also present simultaneously in smaller amounts and has escaped detection. When larger quantities of the substance is available, it is hoped to reinvestigate this question.

Extension of the above reactions to the tricyclic keto-esters (XIII) and (XIV), which are analogous to Hagemann's ester, will eventually lead to the formation of the tricyclic dicarboxylic acids (XV) and (XVI), with the two carboxyl groups most likely in the *trans* position. By preferential double homologation of the secondary carboxyl group, followed by Dieckmann condensation of the adipate, the cyclopentane ring (ring D) can be smoothly developed being fused in the *trans* position with the ring C. This part of the scheme is similar to the method employed by Bachmann for the synthesis of *trans*-8-methylhydrindanone from *trans*-1-methylcyclohexane-1:2-dicarboxylic acid (Bachmann and Kushner, *loc. cit.*).

The required tricyclic keto-esters (XIII) and (XIV) with *trans* fusion of the rings B/C can be readily prepared from the $\alpha\beta$ -unsaturated ketones (XI) and (XII) and ethyl acetoacetate, following the method of preparing ethyl *trans*-4-keto-2-methyl- $\Delta^{2:3}$ -octahydronaphthalene-1-carboxylate (VI) from acetylcyclohexene and ethyl acetoacetate (cf. Barrett, Cook and Linstead, *loc. cit.* See Part III, this issue, p. 373).





EXPERIMENTAL

Ethyl 4-Keto-2-methyl-Δ^{2,3}-cyclohexen-1-carboxylate (Hagemann's ester) was prepared essentially following the procedure described by Rouault and Smith (*loc. cit.*), but a smaller amount of piperidine was employed than that recommended by the above authors. The reaction proceeded with equal facility when this slight modification was introduced and the yield of the final product was unaffected. The following proportion of the reactants were used: ethyl acetoacetate (156 g.), *para*formaldehyde (18 g.) and piperidine (4 c.c.). The average yield was 54-56 g.

Ethyl 3-Methyl-3-cyanocyclohexanone-4-carboxylate (II).—A solution of Hagemann's ester (28.5 g) in rectified spirit (100 c.c.), cooled in an ice-bath, was treated with a solution of potassium cyanide (21.3 g.) in water (52 c.c.). To the yellow solution, after standing for 30 minutes, glacial acetic acid (9.8 g.) was added from a dropping funnel the end of which reached the bottom of the liquid. The reaction mixture was left overnight (20-24 hours) in a refrigerator. The brown solution was poured into water and extracted with ether and the extract was washed twice with water and dried over anhydrous sodium sulphate. The residue after removal of ether was fractionated under reduced pressure. After a forerun of the unreacted Hagemann's ester, the hydrocyanic acid addition product distilled between 130° and 145°/3 mm., which on redistillation boiled at 135°-138°/3 mm. as a pale yellow, mobile liquid, yield 12 g. (Found: N, 6.1, 6.77. C₁₁H₁₅O₃N requires N, 6.7 per cent).

The *semicarbazone* of the nitrile crystallised from alcohol in clusters of glistening needles, m. p. 206°. (Found: N, 22.0. C₁₂H₁₄O₃N₂ requires N, 21.05 per cent).

Ethyl 3-Methylcyclohexanone-3: 4-dicarboxylate (III, R=Et).—The above keto-nitrile (II, 8 g.), dissolved in absolute alcohol (30 c.c.), was treated with alcohol (10 c.c.)

saturated with dry hydrogen chloride gas at 0° . The mixture was left overnight at the ordinary temperature and then refluxed on a steam-bath for 5 to 6 hours. Ammonium chloride separated at the bottom of the flask. The solution was then poured into cold water and the oil taken up in ether. The ether extract was washed with dilute bicarbonate of soda solution, water and dried. The residue left on removal of the ether was distilled and the fraction boiling between 130° and $140^{\circ}/3$ mm. was collected. On redistillation, it boiled at 135° - $137^{\circ}/3$ mm. as a colourless, mobile liquid, yield 4 g. A higher boiling residue was left in the distilling flask. (Found: C, 61.7; H, 8.0. $C_{13}H_{20}O_5$ requires C, 60.94; H, 7.81 per cent).

The *semicarbazone* was crystallised from dilute methyl alcohol, m. p. 158° . (Found: N, 13.59. $C_{14}H_{23}O_5N_3$ requires N, 13.41 per cent).

Ethyl 1-Methylcyclohexane-1:2-dicarboxylate (IV).—The above keto-ester (3.5 g.), dissolved in absolute alcohol (20 c.c.), was taken in a flask containing amalgamated zinc (18 g.). Absolute alcohol (30 c.c.), saturated with dry hydrogen chloride at 0° , was then added to the above solution. After the initial vigour of the reaction was over, the flask was heated on a water-bath for about 6 hours, and again alcoholic hydrogen chloride (15 c.c.) was added and the heating continued for 18 hours more. The solution was then poured into cold water and extracted with ether. The ether extract was then washed with dilute bicarbonate of soda solution, water and dried. The oil left on evaporation of the ether was distilled under diminished pressure, when the dihydro-ester distilled at 107° - $109^{\circ}/3$ mm. as a colourless, mobile liquid, yield 2.5 g. (Found: C, 64.18; H, 8.92. $C_{13}H_{22}O_4$ requires C, 64.46; H, 9.1 per cent).

trans-1-Methylcyclohexane-1:2-dicarboxylic Acid (V).—The above ester (2 g.) was boiled under reflux with concentrated hydrochloric acid (40 c. c.) for 24 hours. The acid separated from the cold solution in colourless sandy crystals which after drying was crystallised from hot water containing a little acetone, m. p. 213° , with previous softening at 210° . The mixed melting point with an authentic specimen of *trans-1-methylcyclohexane-1:2-dicarboxylic acid* was not depressed. (Found: C, 57.98; H, 7.8. $C_9H_{14}O_4$ requires C, 58.06; H, 7.5 per cent).

The *trans*-acid was also obtained when the above keto-ester (III, R=Et, 1 g.) was reduced with amalgamated zinc (5 g.) and concentrated hydrochloric acid (10 c. c.) for 20 hours with the addition of a little hydrochloric acid from time to time. The acid was isolated in the usual manner and crystallised from hot water containing a little acetone, m. p. 213° .

Ethyl trans-4-keto-2-methyl- $\Delta^{2:8}$ -octahydronaphthalene-1-carboxylate (VI) was prepared from acetylcyclohexene and ethyl sodioacetoacetate following the description of Barrett, Cook and Linstead (*loc. cit.*); however, with the slight variation described here a better yield was attained.

Acetylcyclohexene required for this purpose was prepared from cyclohexene nitrile and methylmagnesium iodide following the condition of Butenandt and Schmidt-Thome (*Ber.*, 1938, 71, 1487). To a Grignard reagent prepared from magnesium (10.5 g.),

methyl iodide (36 c. c.) and dry ether (200 c. c.), *cyclohexene nitrile* (45 g.) was added dropwise in the course of about 15 minutes. The ether was then gradually distilled off and replaced by dry benzene (150 c. c.), and the solution refluxed on a steam-bath for 6 hours. After cooling, glacial acetic acid (45 c. c.) was gradually added and the mixture refluxed for 30 minutes. Water was then added and the solution heated for 30 minutes more. The benzene layer was washed with water and dried over anhydrous sodium sulphate. The residue from the benzene solution was distilled under reduced pressure, when *acetylcyclohexene* came over at 80-82°/9 mm., yield 28 g.

To the sodio salt, prepared from ethyl acetoacetate (30 g.), sodium (4.6 g.) and absolute alcohol (60 c.c.), cooled in a freezing mixture, *acetylcyclohexene* (24 g.) was added and the mixture left as such at the room temperature for three days. It was then heated on a steam-bath for 3 hours. After removing the excess of alcohol, the mixture was decomposed with glacial acetic acid and extracted with ether. The ether extract was washed with cold dilute caustic soda solution, water and dried. Ether was then evaporated off and the residue distilled under reduced pressure. The condensation product distilled at 180°/9 mm. as a pale yellow liquid, yield 16 g.

Ethyl 3-Methyl-3-cyanodecalone-4-carboxylate (VII).—A solution of ethyl *trans*-4-keto-2-methyl- $\Delta^{2:3}$ -octahydronaphthalene-1-carboxylate (10 g.) in rectified spirit (50 c. c.) was treated with a solution of potassium cyanide (6 g.) in water (15 c. c.), followed by the addition of glacial acetic acid (2.5 c. c.) exactly in the manner described earlier. After allowing the reaction mixture to remain in the refrigerator for about 30 hours, it was worked up in the usual manner and distilled. After careful removal of the unreacted material, the addition product (VII) was collected between 175° and 185°/1.5 mm. distilling almost constantly at 176°-178°/1.5 mm. as an almost colourless viscous liquid. The product did not solidify when left as such in a vacuum desiccator, but on trituration with a little alcohol the nitrile very readily solidified. It crystallised from methyl alcohol in beautiful, colourless, silky needles, m. p. 116-117°, yield 3 g. (Found: N, 5.16. $C_{18}H_{21}O_3N$ requires N, 5.32 per cent).

The nitrile was subjected to careful fractional crystallisation but so far the product appeared to be quite homogeneous.

Ethyl 3-Methyldecalone-3:4-dicarboxylate (VIII, R=Et).—The above crystalline keto-nitrile (2.5 g.), dissolved in absolute alcohol (10 c. c.), was treated with alcohol (20 c. c.), saturated with dry hydrogen chloride gas at 0°, and left overnight. Next day, it was refluxed for 10 hours on a steam-bath when separation of ammonium chloride took place. The resulting keto-ester was worked up in the usual manner and it distilled at 178°-182°/2 mm. as a colourless, highly viscous liquid. (Found: C, 66.38; H, 8.7. $C_{17}H_{20}O_2$ requires C, 65.81; H, 8.4 per cent).

The keto-ester (1 g.) was heated under reflux on a wire gauze for about 30 hours with amalgamated zinc (25 g.) and concentrated hydrochloric acid (20 c. c.); small quantities of hydrochloric acid (30 c. c. in all) was added to the above solution from time to time. The solution was then extracted with ether after saturation with ammonium chloride. The extract was then extracted twice with dilute bicarbonate of soda solution. The

bicarbonate extract was then very carefully acidified, when a solid together with a little adhering oil separated. After drying overnight in a vacuum desiccator, the acid was first crystallised from ethyl acetate-petroleum ether mixture and then twice from hot water containing a little acetone. m. p. 202-204°. (Found : C, 61.81 ; H, 7.51. $C_{13}H_{18}O_3$ requires C, 61.41 ; H, 7.1 per cent. $C_{13}H_{20}O_4$ requires C, 65.0 ; H, 8.3 per cent). The acid is probably the keto-dicarboxylic acid (VIII, R=H), the carbonyl group having escaped reduction.

The author's grateful thanks are due to Dr. P. C. Mitter, Palit Professor of Chemistry (Retd.), Calcutta University and to Prof. S. N. Bose, for their keen interest and encouragement during the course of this investigation. The author is also grateful to Prof. W. L. Bachmann of the University of Michigan for a gift of an authentic specimen of *trans*-1-methylcyclohexane-1:2-dicarboxylic acid, to Dr. P. C. Dutt, D. Sc., for a gift of chemicals and to Mr. C. N. Bhar, M. Sc. for the microanalysis of a few compounds.

DEPARTMENT ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY,
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STEROID COMPOUNDS. PART III. STUDIES IN THE MICHAEL
CONDENSATION OF 1-ACETYL-3:4-DIHYDRONAPHTHALENE
AND ACETOACETIC ESTER*

BY PRATUL CHANDRA MUKHARJI.

Michael condensation of 1-acetyl-3:4-dihydronaphthalene with ethyl sodio-acetoacetate leads to the formation of ethyl 4-keto-2-methyl- $\Delta^{2:3}$ -hexahydrophenanthrene-1-carboxylate, showing that during the formation of the third ring, ring-closure involves the keto group of the acetoacetic ester residue.

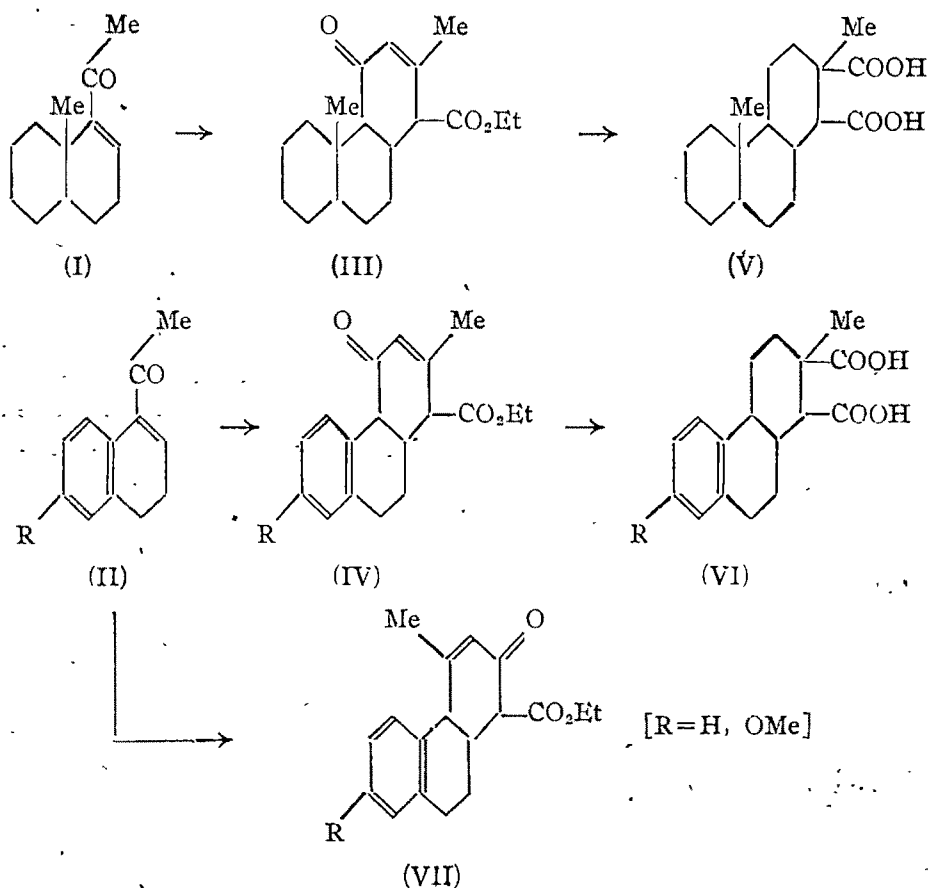
In Part II of this series (this issue, p. 365) it has been pointed out that starting from the tricyclic keto-esters (III) and (IV, R=OMe) it may be possible to prepare the dicarboxylic acids (V) and (VI, R=OMe), where the two carboxyl groups in all likelihood may appear in the *trans* configuration. Following the method employed by Bachmann and Kushner (*J. Amer. Chem. Soc.*, 1943, **65**, 1963) to prepare *trans*-8-methylhydri-danone from *trans*-1-methylcyclohexane-1:2-dicarboxylic acid, it may be possible ultimately to synthesise steroid ketones with the rings C/D fused in the *trans* position, starting from the above dicarboxylic acids. The present work has been carried out with a view to finding out a general method for the synthesis of the required type of tricyclic keto-esters (III) and (IV, R=OMe).

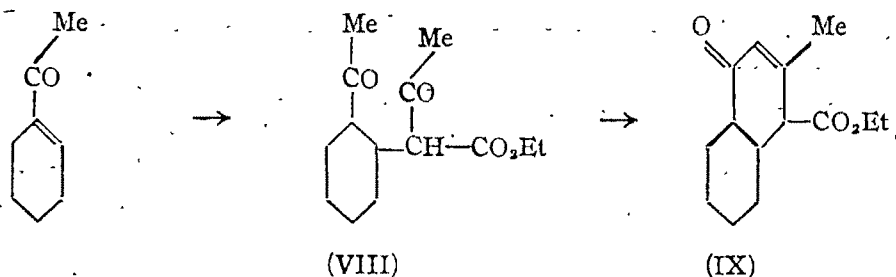
Barrett, Cook and Linstead (*J. Chem. Soc.*, 1935, 1066) have already shown that Michael's reaction of acetylcyclohexene and ethyl sodioacetoacetate leads to the formation of ethyl *trans*-4-keto-2-methyl- $\Delta^{2:3}$ -octahydrophenanthrene-1-carboxylate (IX). The appearance of this compound demonstrates that ring-closure of the intermediate diketone (VIII) first formed involves the carbonyl group of the acetoacetic ester moiety in preference to the other carbonyl group which is comparatively hindered, possibly due to the proximity of the cyclohexane residue. A preliminary study has therefore been made with the readily available 1-acetyl-3:4-dihydronaphthalene (II, R=H) in order to see if the reaction with ethyl sodioacetoacetate pursue the above course to yield the tricyclic keto-ester (IV, R=H) of the required type. Besides the simplicity of this method, a further advantage lies in the fact, that the above reaction leads to the *trans* fusion of the two cycloparaffin rings (Barrett, Cook and Linstead, *loc. cit.* Ruzicka, Koolhaas and Wind, *Helv. Chim. Acta*, 1931, **14**, 1151; Hüchel, *Annalen*, 1925, **441**, 1) exactly as is necessary for the ultimate end in view. The results of this preliminary study confirm that the ring-closure in this case also involves the keto group of the acetoacetic ester residue, as has been found in the reaction between acetylcyclohexene and acetoacetic ester. It can be reasonably anticipated therefore that in the case of 6-methoxy-1-acetyl-3:4-dihydronaphthalene (II, R=OMe) and 9-methyl-1-acetyl- $\Delta^{1:2}$ -octahydronaphthalene (I), the reaction with ethyl sodioacetoacetate will pursue the course observed in the above cases.

* A preliminary note was published in the *Science & Culture*, 1947, **13**, 39.

1-Acetyl-3:4-dihydronaphthalene (II, $R=H$; cf. Birch and Robinson, *J. Chem. Soc.*, 1944, 503) has been prepared from 3:4-dihydronaphthoyl chloride and cadmium dimethyl. The Michael reaction of ethyl sodioacetoacetate with the above ketone proceeds smoothly to yield a highly crystalline phenanthrene derivative which may be represented by either of the structures (IV, $R=H$) or (VII, $R=H$). The compound appears to be stereochemically pure and possibly belongs to the *trans* series as can be deduced from its method of formation. On catalytic hydrogenation of the double bond of this phenanthrene derivative, followed by hydrolysis with concentrated hydrochloric acid, a solid acid (m. p. $187-89^\circ$) is obtained, the formation of which conclusively proves that in this case also the ring-closure as expected involves the carbonyl group of the acetoacetic ester residue to yield the desired compound (IV, $R=H$). Had the ring-closure pursued the other possible route to produce the isomeric compound (VII, $R=H$), then the corresponding dihydro-ester, being β -keto ester derivative, would have suffered decarboxylation during hydrolysis to yield a neutral ketone. In keeping with this, it has also been found that the phenanthrene derivative (IV, $R=H$) as well as its dihydro derivative do not produce any coloration with ferric chloride in alcoholic solution.

Experiments are now well under way for the synthesis of the tricyclic keto-ester (III) and (IV, $R=OMe$).





EXPERIMENTAL

1-Acetyl-3:4-dihydronaphthalene (II, R=H).—This ketone was prepared from 3:4-dihydro-1-naphthoyl chloride and cadmium dimethyl (cf. Carson and Prout, *J. Amer. Chem. Soc.*, 1944, **66**, 46). To a Grignard reagent, prepared from methyl iodide (36 g.), magnesium (6 g.) and ether (90 c.c.), cooled in ice was added in one portion anhydrous powdered cadmium chloride (10.8 g.). After removal from ice-bath the mixture was stirred for 5 minutes and the ether distilled off on a steam-bath, to get a dark semisolid mass. Dry benzene (50 c.c.) was then added and distillation resumed till benzene ceased to distil. Dry benzene (50 c.c.) was then added and the mixture vigorously stirred to get the solid uniformly dispersed in the medium. The acid chloride (27 g.), prepared from 3:4-dihydro-1-naphthoic acid (Sowinski, *Ber.*, 1891 **24**, 2357) and thionyl chloride according to Birch and Robinson (*loc. cit.*) in benzene (30 c.c.); was then added to the above benzene solution, cooled in ice during the course of about 10 minutes with continuous stirring. After about 15 minutes, the mixture was refluxed for 1 hour and the complex decomposed with iced sulphuric acid. The benzene solution was separated and washed with water, dilute bicarbonate of soda solution and benzene removed under reduced pressure. The residue was then heated on a steam-bath with 10% caustic soda solution for 5-10 minutes. The product was then isolated in the usual manner and distilled. The ketone distilled at 160°-165°/10 mm. as a pale yellow oil, yield 16 g. (Found: C, 83.1; H, 6.8. $C_{15}H_{12}O$ requires C, 83.7; H, 7.0 per cent). The *semicarbazone* after crystallisation from alcohol melted at 206°-208° (Birch and Robinson, *loc. cit.*, m. p. 208°).

Michael's Condensation of 1-Acetyl-3:4-dihydronaphthalene with Ethyl Acetoacetate: Formation of Ethyl 4-Keto-2-methyl-Δ²:³-hexahydrophenanthrene-1-carboxylate (IV, R=H).—The above unsaturated ketone (15 g.) was added to the sodio salt of ethyl acetoacetate, prepared from acetoacetic ester (21 g.), sodium (2.1 g.) and absolute alcohol (24 c.c.), cooled in ice bath. The mixture was left at the ordinary temperature for 5 days when a reddish brown thick solution was obtained. It was then heated on a steam-bath for 3 hours, cooled and decomposed with iced acetic acid. The ether extract of the heavy oil was washed with water, dilute caustic soda solution, again with water and dried. From the viscous oil obtained after the evaporation of the solvent, ethyl acetoacetate was removed by distillation under diminished pressure, and the residue on treatment with dilute alcohol gave beautiful silky needles, and was recrystallised from alcohol, m. p. 102°-103°, yield 6 g. (Found: C, 75.56; H, 7.13. $C_{18}H_{20}O_3$ requires

C, 76.05; H, 7.04 per cent). The product did not produce any coloration with alcoholic ferric chloride.

Catalytic Hydrogenation of the above compound: Formation of Ethyl 4-Keto-2-methyloctahydrophenanthrene-1-carboxylate.—A suspension of the above unsaturated keto-ester (4 g.) in absolute alcohol (20 c.c.) was shaken in an atmosphere of hydrogen in presence of Adam's catalyst (0.1 g.). Absorption of hydrogen took place very rapidly and with the progress of hydrogenation the crystals gradually passed into solution. After the theoretical amount of hydrogen had been taken up, the clear alcoholic solution was filtered off, alcohol removed under reduced pressure, and the residue distilled. The dihydro-ester boiled at 183° - $185^{\circ}/4$ mm. as a colourless, viscous oil which did not solidify. (Found: C, 75.1; H, 7.9. $C_{18}H_{22}O_3$ requires C, 75.52; H, 7.7 per cent). It did not produce any coloration with alcoholic ferric chloride. The oxime prepared by the alcohol-pyridine method crystallised from methyl alcohol in clusters of silky needles, m. p. 217° .

Hydrolysis of the above Dihydro-ester.—The above dihydro-ester (2 g.) was refluxed on a wire gauze with excess of concentrated hydrochloric acid for 20 hours. The ether extract of the gummy product was washed three times with dilute bicarbonate of soda solution. After drying over anhydrous sodium sulphate, the ether was distilled off. No appreciable residue remained behind in the flask after the removal of the ether.

The bicarbonate extract was then carefully acidified, when an oily substance separated which, however, solidified after some time. The solid was dried overnight in a vacuum desiccator and then crystallised from a mixture of ether and petroleum ether and subsequently from dilute methyl alcohol, m. p. 187 - 89° with previous shrinking at 177° . (Found: C, 73.82; H, 7.2. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0 per cent).

The author's grateful thanks are due to Dr. P. C. Mitter and Prof. S. N. Bose for their keen interest and encouragement during the course of this investigation, to Dr. P. C. Dutt, D.Sc. for a gift of the starting materials and to Mr. N. Ghosh M.Sc. for the microanalysis of some of the compounds.

DEPARTMENT OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY,
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STUDIES IN FRIES MIGRATION. PART III. THE FRIES MIGRATION OF QUINOL ESTERS

BY GUNVANT CHANDULAL AMIN AND NARSINH MULJIBHAI SHAH

The Fries migration of various quinol esters, viz., quinol diacetate, dipropionate, di- and monobenzoates has been systematically studied for the first time. The effect of various factors such as the amount of anhydrous aluminium chloride, the reaction time, solvent and temperature on the course of the migration has been investigated. No migration could be effected unless the amount of aluminium chloride used was 3.3 mols. As a result, satisfactory method for preparation of quinacetophenone and quinpropio-phenone, otherwise obtained in poor yields, has been evolved. In case of quinol dibenzoate, the reaction becomes complicated as the temperature at which the migration is carried out, is increased, and besides the main product, 2-hydroxy-5-benzoyloxybenzophenone, several other products are formed. In no case a diketone was isolated.

The work described in the previous parts of this series (Thakor and Shah, *J. Indian Chem. Soc.*, 1946, **23**, 199, 234) mainly concerned the Fries migration in the coumarin derivatives. In the present investigation, it has been extended to various quinol esters; quinol diacetate, dipropionate and mono- and di-benzoates have been investigated.

No systematic work has been done so far to study the Fries migration of quinol esters. It has been reported that quinol diacetate does not undergo the Fries transformation under the usual experimental conditions (Heller, *Ber.*, 1912, **45**, 2389; Mauthner, *J. prakt. Chem.*, 1934, *ii*, **139**, 293). However, Rosenmund and Lohfert (*Ber.*, 1928, **61**, 2602) and recently Desai and Mavani (*Curr. Sci.*, 1941, **10**, 524) and Shahane (*ibid.*, p. 523) have reported that the above migration is possible under certain conditions. The higher quinol esters like quinol distearate, 4-methoxyphenyl palmitate and stearate do not undergo this migration (Cook, Heilbron and Lewis, *J. Chem. Soc.*, 1942, 659; Cruickshank and Robinson, *ibid.*, 1938, 2064). Incidentally it may be noted that the diacetate of 2-methoxyquinol smoothly migrates yielding the expected product, 2:5-dihydroxy-4-methoxyacetophenone (Mauthner, *J. prakt. Chem.*, 1933, *ii*, **136**, 205), whereas quinol itself does not undergo the Friedel-Crafts or Hoesch reaction; it reacts under the conditions of the Nencki reaction yielding quinacetophenone in a poor yield (Nencki and Schmid, *ibid.*, 1881, *ii*, **23**, 546). Russel and Clarke (*J. Amer. Chem. Soc.*, 1939, **61**, 2654) obtained a slightly better yield (20-25%) by a modified Nencki procedure.

In the present work, we have investigated the effect of various factors on the course of the Fries migration of quinol diacetate. For the sake of brevity, the results of various experiments under different conditions are presented in a tabular form (Table I). It has led us to evolve the best conditions for the preparation of quinacetophenone (II, R=Me) from quinol diacetate (I, R=Me) in good yield.

TABLE I

Fries migration of quinol diacetate

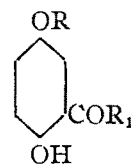
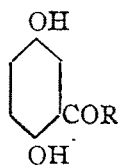
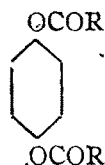
Quinol diacetate used in each experiment = 5 g.

Expt. No.	Temp.	Time.	Amount of AlCl_3 .	Products	
				Unchanged quinol diacetate.	Quinacetophenone.
1	85°-90°	4 hours	3.3 M	3.0 g.	...
2	120°-130°	4	3.3	2.5	0.5 g.
3	140°-160°	4	3.3	...	2.7
4	"	1	3.3	...	2.2
5	"	4	3.3 (60 c.c. $\text{C}_6\text{H}_5\text{NO}_2$)
6	"	4	3.3 (30 c.c. CS_2 for mixing)	...	2.1
7	"	4	2.2 M	2.5	...
8	"	4	1.1	3.1	...
9	"	4	5.5	...	2.7
10	170°-180°	4	3.3	...	1.5
11	"	4	2.2	2.2	Trace
12	"	1	3.3	...	1.3
13	20°-25°	24	3.3 (60 c.c. $\text{C}_6\text{H}_5\text{NO}_2$)

(1) All the experiments recorded here were repeated several times and concordant results were obtained.

(2) In all the experiments after the products were separated, a small quantity of a black tarry material was always left behind. It could not be purified.

The same conditions (the temperature has to be carefully regulated to 140°) were also found to be applicable in the case of migration of quinol dipropionate (I, R = Et).



The Fries migration of benzoyl esters of quinol has practically remained uninvestigated. By analogy with quinol diacetate and dipropionate; the migration of quinol di-benzoate was expected to yield quinbenzophenone. The expectation was not realised;

instead of quinbenzophenone, however, it afforded a product of m. p. 94° - 95° accompanied with the original dibenzoate. The product has been identified to be 2-hydroxy-5-benzoyloxybenzophenone (III, $R = \text{COPh}$; $R_1 = \text{Ph}$) on the following considerations: (i) It is soluble in alkali indicating free $-\text{OH}$ group and further, it gives ferric chloride colour test indicating $-\text{OH}$ and $-\text{COPh}$ groups in *ortho* positions; (ii) its benzoyl derivative has the same melting point as the dibenzoyl derivative of quinbenzophenone, the mixed melting point with an authentic sample remaining unchanged; (iii) on hydrolysis by concentrated sulphuric acid, quinbenzophenone was produced (Bogert and Howells, *J. Amer. Chem. Soc.*, 1930, **52**, 840; cf. Klinger and Standke, *Ber.*, 1891, **24**, 1340).

In course of the further work, it has been found that 2-hydroxy-5-benzoyloxybenzophenone is the main product of the reaction. For the sake of brevity, the results of all the experiments under different conditions are given in Table II.

TABLE II

Fries migration of quinol dibenzoate

Quinol dibenzoate used in each experiment = 3 g.

Exp. No.	Temp.	Time.	Amount of AlCl_3	Quinol dibenzoate.	Monobenzoyl quinbenzophenone.	Quinol monobenzoate.
1	120°	1 hr	3.3M	2.2 g.	Trace	...
2	120°	4	3.3	1.9	Trace	...
3	140°	3	3.3	1.2	0.3 g.	...
4	140°	4	3.3+1.1 g. quinol	0.6
5	140°	4	3.3+0.6 g. quinol	1.0	Trace	0.2 g.
6	140°	1	3.3	0.3	1.0 g.	...
7	140°	3	3.3+40 c.c. $\text{C}_6\text{H}_5\text{NO}_2$
8	20° - 25° (room temp.)	24	3.3+40 c.c. $\text{C}_6\text{H}_5\text{NO}_2$	1.2
9	140°	1	1.1M	2.5
10	140°	1	2.2	2.3
11	140°	1	5.5	0.3	1.0 g.	...
12	150° - 155°	3	3.3	0.4	0.4	0.4 g.
13	180°	1	3.3	0.2	0.3	0.3
14	200° - 205°	1	3.3	0.2	0.2	0.4
15	"	1	5.5	0.2	0.2	0.3

(1) In the experiments 13, 14 and 15, 0.3 g. of quinbenzophenone was isolated, in addition to the products mentioned.

(2) In experiments 8, 13 and 14, traces of quinol were obtained from ether extracts of the mother-liquor after other products were separated off.

(3) In experiment 7, no definite product could be isolated, only charred mass was produced.

It will be seen that the migration becomes complex as the temperature is raised. At 180° a small quantity of quinbenzophenone along with the other products is isolated. At higher temperature, much pasty mass is obtained. It is noteworthy that the reaction is not simple migration at higher temperatures. Besides, monobenzoyl quinbenzophenone, quinol monobenzoate, quinbenzophenone, quinol and its dibenzoate are among the other products which have been isolated. Incidentally, it may be mentioned that in no case a diketone was isolated.

The migration of quinol monobenzoate was expected to produce quinbenzophenone in good yield, but actually the migration was found complicated. Here also, 2-hydroxy-5-benzoyloxybenzophenone was found to be the main product. However, in all cases quinol dibenzoate was isolated in appreciable quantity. In no case, either quinbenzophenone or a diketone could be isolated. The results of the various experiments are shown in Table III.

TABLE III

Fries migration of quinol monobenzoate

Quinol monobenzoate used in each experiment = 2.1 g. Amount of AlCl_3 used in each experiment = 4.4 g. (3.3 mols).

Exp. No.	Temp.	Time.	Quinol dibenzoate.	Monobenzoyl quinbenzophenone.	Quinol monobenzoate.
1	120°	1 hr.	0.3 g.	...	0.6 g.
2	120°	4	0.3	...	0.4
3	140°	1	0.4	0.3g.	0.2
4	140°	4	0.4	0.2	0.2
5	160°-170°	1	0.2	0.1	Trace
6	200°	1	0.1

In all experiments a variable amount of blackish residue remained after isolation of the different crystalline products.

EXPERIMENTAL

Preparation of Quinol Esters

Quinol diacetate was prepared by the following method which gave a satisfactory yield. Acetic anhydride (102 g., 2 M) was gradually added to the solution of quinol (55 g., 1.0 M) in sodium carbonate solution (110 g. in 1650 c. c. water) over a period of half an hour. The mixture was mechanically stirred all the while. After the addition was over, the precipitated diacetate was allowed to settle. It was filtered, washed with cold water and crystallised from alcohol, m. p. 123-24°, yield 78-80 g.

Quinol Dipropionate.—Propionic anhydride (19.5 g., 1.5 M), followed by ice (about 50 g.), was quickly added to the solution of quinol (11 g., 1 M) in 60% sodium hydroxide solution (10 c. c.). The solid that immediately separated, was collected and crystallised from alcohol in thin, lustrous plates, m. p. 112-13°, yield 15-16 g.

Quinol-dibenzoate was prepared by the usual Schotten-Baumann method, m. p. 200-201°.

Quinol monobenzoate was prepared according to the method of Witt and Johnson (Ber., 1893, **26**, 1908), m. p. 162-63°. A small quantity of quinol dibenzoate was also obtained as alcohol-insoluble residue.

The Fries migrations of the different esters were carried out by the same general method described in Part I of this series (J. Indian Chem. Soc., 1946, **23**, 201).

Preparative Method for Quinacetophenone.—An intimate mixture of quinol diacetate (50 g.) and aluminium chloride (110 g.) was heated at 140°-160° for 4 hours. After decomposing the reaction mixture by ice and hydrochloric acid, the solid was collected and crystallised from alcohol in greenish needles, m. p. 201°-202°, yield 25-30 g.

Fries Migration of Quinol Dipropionate.—The ester (25 g.) and aluminium chloride (50 g.) were intimately mixed and heated for 4 hours at 130°-140°. The product was decomposed by ice and hydrochloric acid and the solid after filtration was crystallised from hot water in fine needles, m. p. 91-92°, yield 14 g.

*Isolation of the different Products from the Migration mixture of
Quinol Dibenzoate*

Experiment No. 13 in Table II is described in details as a typical experiment.

The mixture of aluminium chloride and ester was heated as outlined in the general method. The solid obtained on decomposition of the reaction mixture was extracted with hot water. The aqueous solution (A) and the residue (B) were separately examined.

(A). The aqueous extract on cooling deposited needles, m. p. 110-20°. The needles were redissolved in boiling water and allowed to cool to about 75°-80°. The crystals separating were filtered off and recrystallised from water, m. p. 162-63° (small quantity). It was identified as quinol monobenzoate by the mixed melting point with an authentic sample. The filtrate on further cooling gave flat needles, which on recrystallisation melted at 124-25°. The product was identified as quinbenzophenone. (Found : C, 72.51 ; H, 4.62. Calc. for $C_{15}H_{10}O_3$: C, 72.9 ; H, 4.67 per cent).

Quinbenzophenone is soluble in sodium hydroxide and concentrated sulphuric acid with dark red colour and gives dark green colour with alcoholic ferric chloride. It is soluble in all common solvents and hot water. It reduces ammoniacal silver nitrate and Fehling's solution.

The mother-liquor, after separation of quinol monobenzoate and quinbenzophenone, gave on extraction with ether brown residue containing some white needles. Some of the needles were picked up and identified as quinol, m. p. 169-70° (mixed m. p. with a Merck's sample).

(B). The insoluble residue was extracted with alcohol. The alcoholic extract gave greenish yellow needles, m. p. 94-95°, which were identified as monobenzoyl quinbenzophenone. (Found : C, 75.61 ; H, 4.46. $C_{20}H_{14}O_4$ requires C, 75.47 ; H, 4.4 per cent).

Monobenzoyl quinbenzophenone is soluble in all common organic solvents but insoluble in hot water. It dissolves in sodium hydroxide with deep red colour. With alcoholic ferric chloride it gives a dark green coloration.

The mother-liquor, after separation of monobenzoyl quinbenzophenone, was diluted and the brown solid obtained was crystallised from water, m. p. 162-63°. It was quinol monobenzoate.

The insoluble alcoholic residue after crystallisation from acetic acid was found to be quinol dibenzoate, m. p. 200°-201°.

The *acetyl derivative* of monobenzoyl quinbenzophenone was prepared by sodium acetate method and crystallised from alcohol in colourless needles, m. p. 94-95°. The mixed melting point with the original ketone was depressed to 76-78°. (Found : C, 72.81 ; H, 4.58. $C_{22}H_{16}O_3$ requires C, 73.33 ; H, 4.44 per cent).

The *benzoyl derivative*, prepared by Schotten-Baumann method, melted at 117-18° (mixed m. p. with the dibenzoyl derivative of quinbenzophenone). (Found : C, 76.56 ; H, 4.10. $C_{27}H_{18}O_3$ requires C, 76.77 ; H, 4.26 per cent).

Hydrolysis of Monobenzoyl quinbenzophenone.—The ketone (1 g.) was kept overnight with concentrated sulphuric acid (5 to 7 c.c.). The deep red mixture was poured on ice and the solid obtained was filtered, washed with cold water and crystallised from hot water, m. p. 124-25° (mixed m. p. with quinbenzophenone).

The *dibenzoate*, derived from quinbenzophenone by Schotten Baumann, was prepared by the usual method, m. p. at 117-18°.

The *semicarbazone*, prepared by the usual method, melted at 159-60° (decomp.).

The *dimethoxy* derivative, prepared by means of dimethyl sulphate, crystallised from petrol, m. p. 51-52°. Kaufmann and Grombach (*Ber.*, 1905, 38, 796) give the same melting point.

DISCUSSION

It will be seen from the result that the amount of aluminium chloride required for migration is three mols. without which no migration is possible. With less than three mols. of aluminium chloride, no migration product could be isolated, unchanged ester or pasty mass was obtained. Even at higher temperature, the less amount of aluminium chloride did not promote the reaction. Large quantity of aluminium chloride (5.5 mols.) did not affect either the yield or the course of the reaction.

Aluminium chloride has a tendency to form complexes with compounds containing oxygen atoms; it appears that the extra two mols. are utilized in the complex formation with the hydroxy-ester groups of quinol. Such ester complexes have been actually isolated as intermediate products in many reactions (Gaustavson, *Bull. Soc. chim.*, 1886, ii, 34, 322 ; Perrier, *ibid.*, 1893, iii, 9, 1049 ; Walker and Spencer, *J. Chem. Soc.*, 1904, 85, 1108).

The effect of temperature is important. As the *para* position is occupied, the only possibility is of the *ortho* migration. In no case the migration was observed below 140°. Quinol diacetate on migration yields always quinbenzophenone; in case of dibenzoate and monobenzoate, 2-hydroxy-5-benzoyloxybenzophenone is formed; one of the

two ester groups remaining unaffected. With increase in temperature, yield of quinacetophenone is lowered ; while in the case of benzoyl ester, the reaction becomes complicated and quinol monobenzoate, quinol and quinbenzophenone are produced along with the diminishing yield of 2-hydroxy-5-benzoyloxybenzophenone. The other products may be due to the hydrolysis of the previously formed products at higher temperatures. The presence of quinol dibenzoate even at higher temperatures is interesting. It shows that either the reaction is incomplete or it is formed during the course of the reaction : it shows that it is an intramolecular reaction, since in the migration of quinol monobenzoate, it is invariably isolated. Even when the quantity of aluminium chloride is in large excess (5.5 mols.) and the temperature as high as 200°, quinol dibenzoate is invariably isolated as one of the products. In case of quinol monobenzoate, the material is charred at higher temperatures, but no quinbenzophenone is formed.

In the present work nitrobenzene as a solvent was found to have no beneficial effect but rather it retarded the reaction. This is in contrast to its beneficial effect in many of the migrations studied previously.

It is apparent that the nature of the group plays an important part. The migration of quinol diacetate leads to the dihydroxy ketonic compound, but in case of quinol dibenzoate, one of the two benzoyl groups is firmly held. This is in accord with the view that an aromatic acid residue is more tenaciously held up by the oxygen atom of the phenol molecule than an aliphatic one (Rosenmund and Schnurr, *Annalen*, 1928, **460**, 56). At higher temperature, quinol and quinbenzophenone are formed, but it may be due to the effect of temperature or side reactions. In case of quinol diacetate, no monoacetoxy ketone could be isolated, due to the migration and hydrolysis having taken place simultaneously.

Earlier workers in this field used to prolong the reaction for a very long time, but recently Rosenmund and Schnurr (*loc. cit.*) observed that actually the reaction was over within 15 to 20 minutes. In the present case, the reaction is almost over in the first hour after which the evolution of hydrochloric acid gas slackens. The continuation of heating for a longer period does not increase the yield of quinacetophenone, while in the case of dibenzoate, it is not appreciable as the amount of the product is neither substantially lowered or increased. However, it only increases the amount of pasty residue in the latter case.

From the above discussion, optimum conditions for the migration of quinol diacetate are those given in experiment 3 in Table I and for dibenzoate and monobenzoate are those given in experiments 6 and 3 of Table II and III respectively. These optimum conditions are applicable for the large-scale migration of quinol diacetate and dipropionate but are of no avail in the case of benzoyl esters. With large quantities of the latter esters, the yield of the migrated product is not increased in the same ratio. The suitable method for the preparation of quinbenzophenone appears to be the hydrolysis of monobenzoyl quinbenzophenone, easily obtained by the migration of quinol mono or dibenzoates.

TABLE IV

Effect of heating on the inhibiting power of cobra venom

Conc. of venom in the medium = 0.0033 mg./c.c.

Cu. mm. of oxygen absorbed per g./hr. by

No. of expt	Temp. at which the venom soln. heated for 30 min.	Brain.	Substrate.	Brain + substrate.	Brain + venom.	Brain + venom + substrate.	% Inhibition.
1	30°	316	3	3640	160	1680	54
2	70°	280	4	3040	132	1514	50
3	75°	252	4	3260	130	1620	51
4	80°	272	3	3510	145	1862	47

TABLE V

The tryptic activity of the purified material

0.02 N-KOH required

Material tested.	Conc. of the material in mg./c.c. of the soln	after digestion (I).	Control (II).	Diff. between (I) & (II).
Cobra venom	3.0	3.4 c.c.	2.5 c.c.	0.9 c.c.
Purified material	3.0	2.5	2.5	0.0

TABLE VI

The inhibiting power of the purified material

Cu. mm. of oxygen absorbed per g./hr. by

No. of expt.	Purified material (mg./c.c. of suspension).	Brain.	Substrate.	Brain + substrate.	Brain + venom.	Brain + venom + substrate.	% Inhibition.
1	0.033	242	3	3420	70	388	90
2	0.033	310	4	3670	85	358	92
3	0.033	280	3	3284	82	535	85

Separation of the Inhibitor from Cobra Venom.—The presence of a separate active principle in cobra venom responsible for the inhibition of the cytochrome-cytochrome oxidase system having been established, attempts were made to isolate the inhibitor in a purified state from the crude venom. The inhibitor was separated from the trypsin in the following way.

An 1% solution (100 c.c.) of cobra venom in water was adjusted to p_H 9.0 and treated with 20 g. of pure sodium chloride in small amounts at a time. The solution was kept at 37° for about 30 minutes and then filtered. The filtrate was found to contain the inhibitor. The precipitate was dissolved in 50 c.c. of water, the p_H adjusted to 9.0 and 10 g. of pure sodium chloride were added slowly. The solution was kept at 37° for 30

minutes and filtered. The precipitate was rejected. The filtrates were combined and dilute H_2SO_4 was added to lower the p_H to 2.0. The precipitate formed was separated by filtration and dried in a vacuum desiccator over fused $CaCl_2$. The tryptic activity and the inhibiting power of the dry precipitate have been estimated. Its nitrogen content has also been determined by the micro-Kjeldahl method. The results are recorded in Tables V and VI.

The results recorded in Tables V and VI show clearly that the partially purified material is devoid of any tryptic activity, but possesses quite strong inhibiting action on the cytochrome-cytochrome oxidase system.

CONCLUSION

Cobra venom, in minute doses, can inhibit the cytochrome-cytochrome oxidase system markedly. This is one of the main causes of the inhibition of tissue respiration by cobra venom.

The inhibition of cytochrome-cytochrome oxidase system by the venom is not due to the trypsin present in it.

The inhibitor has been partially purified.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE
AND TECHNOLOGY, CALCUTTA.

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THE AVAILABILITY OF ASCORBIC ACID OF SHADDOCK (*CITROUS DECUMANA*) BY ADULT HUMAN SUBJECTS

By H. N. DE AND S. C. BARAI

The availability of vitamin-C of shaddock was determined by experiments on three healthy students of age 20 to 23 years. Response to doses of ascorbic acid varied from subject to subject. The average urinary excretions of ascorbic acid of the three subjects on a daily dose of 75 mg. of crystalline ascorbic acid were found to be 47.4, 41.3 and 45.7 mg and on a daily dose of 25 mg. of the crystalline acid and 50 mg. vitamin C from shaddock juice. These were found to be 50.2, 41.3 and 44.5 mg. respectively. It is concluded that the availability of vitamin-C of shaddock is of the same order as that of the crystalline ascorbic acid.

Much work has been done regarding the vitamin-C content of Indian fruits, vegetables and other foodstuffs, but there is no literature about their availability by Indian adult. The purpose of the present investigation is to study the availability of vitamin-C of shaddock, a citrous fruit, by direct metabolic experiments on human subjects.

Very little work has been done in this line of human nutrition. Hawley, Stephens and Anderson (*J. Nutrition*, 1936, 11, 135) by studying with orange juice, Todhunter *et al.* (*ibid.*, 1940, 19, 121) with lemon juice and raspberries, Clayton *et al.* (*J. Home. Econ.*, 1940, 32, 390; *J. Nutrition*, 1943, 26, 349) with potato, raw cabbage and canned tomato juice, and Hartzler (*J. Nutrition*, 1945, 30, 355) with papaya and guava found that the vitamin-C of the above foodstuffs was as well utilised as that in pure crystalline form.

'Zambura' or 'Batapi Lebu' (*Citrous decumana*), also called grapefruit, shaddock and pomalo in English, is a cheap citrous fruit found abundantly in India and contains a fairly large amount of ascorbic acid in its juice (45 to 60 mg./100 c.c.). Because of cheapness and the presence of a considerable amount of ascorbic acid in it, this fruit was chosen for the present investigation.

EXPERIMENTAL

The method used in the present study was similar to that adopted by Clayton and Borden (*J. Nutrition*, 1943, 26, 349) with some modifications. In their investigations the subjects were resaturated after the control period before the experimental period, but in the present investigation the subjects were tested for saturation after the completion of the control and experimental periods.

The experiments were carried out in following periods :—

Preliminary adjustment period.—Each subject was given 300 mg. of ascorbic acid* per day for 3 days before starting the experiment, the experimental periods were as follows :

* Redoxon tablets (Roche products) received by the courtesy of Messrs Volkart Brothers, Bombay.

Period-1. Saturation period (duration, 7 days).—The subjects were on the basal diet *plus* 200 mg. of vitamin-C daily (two 50 mg. tablets at breakfast and another two at lunch).

Period-2. Control period (duration, 7 days).—The subjects were on basal diet *plus* 75 mg. of vitamin-C daily at breakfast. The purpose of this period was to determine to what extent saturation could be maintained by 75 mg. of the pure vitamin.

Period-3. Experimental period (duration, 7 days).—The subjects were on basal diet *plus* 25 mg. of vitamin-C and the amount of shaddock juice required to provide 50 mg. of vitamin-C. The purpose of this period was to determine to what extent the vitamin-C of the shaddock juice supplemented by the 25 mg. of vitamin-C in tablet form would maintain saturation and how the results would compare with those secured in period-2.

Period-4. Saturation-test period (duration, 2 days).—The subjects were on basal diet *plus* 200 mg. of vitamin-C daily as in period-1. The purpose of this period was to test if the subjects were in a state of saturation throughout the control and experimental periods.

TABLE I

Urinary excretion (24 hours) of vitamin-C (in mg.)

Periods	Subject No I	Subject No II	Subject No III	Subject No I	Subject No II	Subject No III	Subject No I	Subject No II	Subject No III	Subject No I	Subject No II
	Saturation period			Control period			Experimental period			Saturation test period	
1st day	226.8	103.0	146.5	94.4	45.3	84.0	77.9	58.0	60.0	115.2	94.0
2nd day	105.6	78.1	115.0	45.1	64.0	48.0	72.6	41.0	48.0	130.0	112.5
3rd day	129.9	87.4	152.5	64.4	38.0	60.5	32.5	51.2	58.0	—	—
4th day	149.6	94.6	107.0	45.1	56.0	32.5	58.1	37.0	31.0	—	—
5th day	154.9	114.7	136.4	50.2	31.0	49.0	61.0	42.0	—	—	—
6th day	110.0	103.0	103.5	32.0	45.5	38.5	42.5	33.0	—	—	—
7th day	139.7	108.9	140.5	45.5	36.0	48.0	57.0	43.5	—	—	—
Mean of the last 5 days	136.8	101.7	128.0	47.4	41.3	45.7	50.2	41.3	44.5*		

*The mean value of 3rd and 4th days excretions.

The experiment was conducted on three college students residing in hostel and they were kept on restricted diet providing on average less than 5 mg. ascorbic acid daily. The diet was fed *ad libitum* and consisted of boiled rice, mashur dal, fish, *patol* and boiled cow's milk. Other vitamins were provided in the form of tablets twice daily to supply the requirement. As the vitamin-C content of the shaddock juice varied in almost every fruit, the juices were analysed every day before they were given as experimental doses.

Urine excreted during 24 hours was collected in brown (2500 c.c.) glass-stoppered bottles containing enough oxalic acid to bring the acid concentration of the final volume to 0.5%.

All ascorbic acid determinations were made with 2,6-dichlorophenol-indophenol in the photoelectric colorimeter by the method of Loeffler and Ponting (*Ind. Eng. Chem. Anal. Ed.*, 1942' 14, 846).

DISCUSSION

Results of the experiments are shown in Table I from which it is observed that on ingesting 200 mg. ascorbic acid to the students in the saturation period, immediately after the preliminary adjustment period with 300 mg. dose, the subjects I, II and III during 24 hours excreted 105.6 to 226.8 mg., 78.1 to 114.7 mg. and 103.5 to 152.5 mg. ascorbic acid in urine respectively. Since 300 mg. dose of the preliminary adjustment period might have influenced the urinary excretions of the first two days of the saturation period following it, only the last five days' collection of the saturation period was taken into consideration and their average values 136.8 mg., 101.7 mg. and 128 mg. respectively for the subjects I, II and III have been presented in the table. As these average values were more than 50% of the intake, the subjects were therefore regarded as saturated. Since lower test dose of 200 mg. saturated the subjects, the higher test dose was not applied.

After saturation, when 75 mg. of crystalline ascorbic acid were given in the control period, the daily urinary excretion of ascorbic acid of the subjects I, II and III for the last five days of the period ranged from 32 to 64.4 mg., 31 to 56 mg. and 32.5 to 60.5 mg. with the mean values of 47.4, 41.3 and 45.7 mg. respectively.

In the experimental period, when the subjects were given 25 mg. of crystalline ascorbic acid and a quantity of shaddock juice (generally 80 to 100 c.c.) required to furnish 50 mg. of vitamin-C, the daily urinary output of the vitamin by subjects I and II was found to range from 32.5 to 61.0 mg. and 33.0 to 51.2 mg. with the mean value of 50.2 and 41.3 mg. respectively for the last five days' excretion period. As the subject no III fell ill after the 4th day of the experimental period, the experiment on that subject was discontinued after that day and the average value of 44.5 mg. of the 3rd and 4th days' excretions has been shown in the table.

To test whether the subject remained saturated after the control and experimental periods, they were given 200 mg. test dose of crystalline ascorbic acid for 2 days. The subjects were found to respond to this dose satisfactorily. The urinary excretions of vitamin-C on the 2nd day were found to be 130 and 112.5 mg. for the subjects I and II respectively. As these eliminations exceeded 50% of the total intake, the subjects were considered to have remained saturated during the whole control and experimental periods.

Survey of the data presented in the table shows that the average urinary excretions

of ascorbic acid in the experimental period exceeded that in the control period by +2.8 mg. for subject I, by 0.0 mg. for subject II, and by -1.2 for subject III. The negative value in the case of the subject III may be due to comparatively short experimental period. As the differences in the mean values of the urinary excretion of vitamin-C by the subjects in the experimental and control periods are not large, it may be concluded that the ascorbic acid of shaddock is as well utilised as the crystalline vitamin-C.

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BIOCHEMICAL LABORATORY,
DACCA UNIVERSITY.

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STUDIES ON THE FRIES REARRANGEMENT. PART I

By A. B. SEN AND V. S. MISRA

Fries rearrangement takes place with esters of $\alpha\beta$ -hexenic acid and β -isopropylacrylic acid, but no identifiable product could be isolated from the corresponding reaction with oleic acid.

It was observed by Fries and Fink (*Ber.*, 1908, 41, 4271) that acyl derivatives of phenols, when heated with anhydrous aluminium chloride, were converted smoothly into the isomeric *o*- or *p*-hydroxy-ketones, or more often into a mixture of the two. The chief variation in the results is in the ratio of the *ortho* and the *para* isomers, which is influenced to a great extent by the nature of the solvent, the amount of the catalyst and the temperature at which the reaction is conducted (Barch, *J. Amer. Chem. Soc.*, 1935, 57, 2330; Ralston *et al.*, *J. Org. Chem.*, 1940, 5, 645; Rosenmund and Schnurr, *Annalen*, 1928, 460, 56); as a rule, low temperature favours *para* substitution and high temperature, *ortho* substitution.

Considerable amount of work in this field has been carried out with esters of saturated aliphatic carboxylic acids (cf. Adams, "Organic Reactions," Vol. I, pp. 357-363), but esters of purely aliphatic unsaturated acids do not appear to have been tried, excepting a few esters of cinnamic acid which have been found to rearrange (Rosenmund and Schnurr, *loc. cit.*).

In the present paper this reaction has therefore been extended to esters of three unsaturated acids, viz. $\alpha\beta$ -hexenic acid, β -isopropylacrylic acid and oleic acid.

Six esters of $\alpha\beta$ -hexenic acid with phenol, *o*-, *m*- and *p*-cresol, resorcinol mono-methyl ether and hydroquinone monoethyl ether have been obtained. In the case of β -isopropylacrylic acid only four esters with phenol, *o*-, *m*- and *p*-cresol have been prepared. In the case of oleic acid only three esters, viz. *o*-, *m*- and *p*-cresyl oleate have been prepared.

The main rearrangement products (about 50-60%) of $\alpha\beta$ -hexenic and β -isopropylacrylic esters are *ortho*-hydroxy ketones which have been characterised through their 2:4-dinitrophenylhydrazones. In the case of oleic esters, no identifiable product could be obtained on treatment with anhydrous aluminium chloride owing to the high temperature distillation in vacuum which resulted in dark resinous products.

EXPERIMENTAL

Acids

$\alpha\beta$ -Hexenic acid was prepared according to Auwers' general method (*Annalen*, 1923, 432, 46). *n*-Butyraldehyde (54 g.), malonic acid (78 g.) and pyridine (88.5 g.) were heated together on the water-bath for 6 hours till the evolution of CO₂ had ceased. Pyridine was removed under reduced pressure and the reaction mixture was slowly added to

of the ester was added slowly. The evolution of hydrogen chloride commenced at 60° (external temp.). When the reaction had subsided, the bath temperature was raised to 100° for completing the reaction. To the reddish puffy mass obtained dilute hydrochloric acid was added to decompose the aluminium chloride compound. The oil which separated was extracted with ether, washed successively with water, 1% sodium carbonate solution and finally with water. After dehydration over anhydrous sodium sulphate the ether was distilled off and the residue distilled in vacuum.

The distillate gave an intense red-violet coloration with ferric chloride and on addition of dilute caustic soda a yellowish red precipitate indicating that it is an *o*-hydroxy ketone (cf. Pyman, *J. Chem. Soc.*, 1930, 280).

The *ortho*hydroxy ketones, thus obtained, were all converted into their 2 : 4-dinitrophenylhydrazones which were recrystallised from toluene.

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STUDIES ON THE CIRCULAR DICHROISM AND ROTATORY DISPERSION.
PART IV. MEASUREMENT OF ABSORPTION, CIRCULAR
DICHROISM AND ROTATORY DISPERSION OF
SODIUM VANADYL *d*-TARTRATE

By B. C. KAR AND S. K. ROY

Measurement of absorption, circular dichroism and the rotatory dispersion of sodium vanadyl *d*-tartrate have been carried out. The absorption bands and the circular dichroism and rotatory dispersion associated with the absorption bands have been represented by the empirical equation published by the author in a previous paper (Kar, this *Journal*, 1947, 24, 461).

Studies on the circular dichroism and rotatory dispersion of ammonium vanadyl *d*-tartrate and potassium vanadyl *d*-tartrate have already been made in this laboratory (Kar, *J. Indian Chem. Soc.*, 1945, 22, 278; 1947, 25, 117; 1948, 25, 267). In the present communication the investigation has been extended to sodium vanadyl *d*-tartrate.

EXPERIMENTAL

Sodium vanadyl *d*-tartrate was prepared in the same way as the ammonium salt and potassium salt (Kar, *loc. cit.*). In place of ammonium vanadate, sodium vanadate was taken.

Measurements of absorption, rotation and ellipticity were carried out by the same method and apparatus as described in previous parts and similar results have been obtained.

Analysis of the Absorption Curves.—The extinction coefficients have been calculated by the equation

$$\epsilon = \frac{2 \log \tan \theta}{l}$$

where θ is the spectrophotometric reading and l is the length in cm. and have been tabulated in Table I and are represented graphically in Fig. 1. The molecular extinction coefficient has not been calculated, as the water of crystallisation of the molecule of sodium vanadyl *d*-tartrate is not known to us. The first absorption band is reduced to a 'step out' the maximum of which is very difficult to ascertain, while the second absorption band shows a maximum at about 5172 Å. Attempts have been made to analyse the second absorption band only. The following equations have been used to analyse the second absorption curve.

(a) Equation of Ketteler and Helmholtz

$$\epsilon = \frac{a\lambda^2}{(\lambda^2 - \lambda_m^2)^2 + g^2\lambda^2}$$

where ϵ =extinction coefficient at wave-length, λ ; λ_m =the wave-length corresponding to the head of the band; a and g^2 are constants.

- (b) Equation of Bielecki and Henri (*Physikal. Z.*, 1913, **14**, 516).
- (c) Equation of Kuhn (*Z. physikal. Chem.*, 1929, **4**, 14; *Trans. Faraday Soc.*, 1930, **26**, 293).
- (d) Equation of Kuhn and Braun (*ibid.*, 1930, **8**, 281).
- (e) Equation of Lowry and Hudson (*Phil. Trans.*, 1933, **A**, 232, 117).
- (f) Equation of Kar (*J. Indian Chem. Soc.*, 1947, **24**, 461).

The extinction coefficients calculated from those six equations are tabulated in Table I. It is interesting to note that our equation represents the experimental data better than any other equations.

FIG. 1

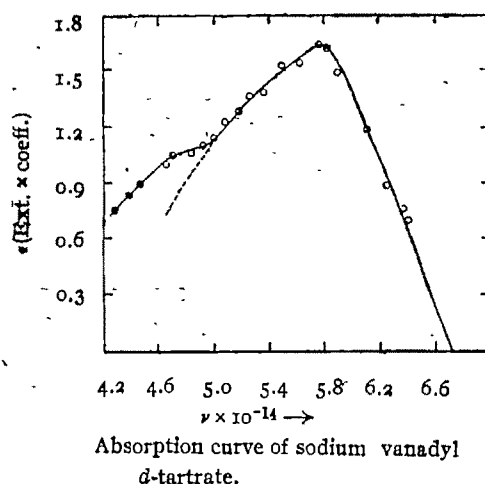
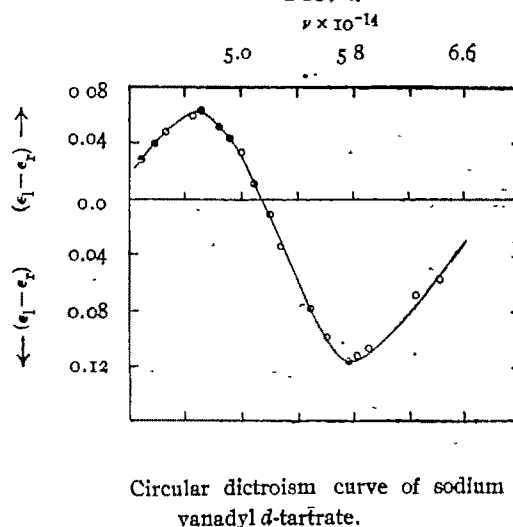


FIG. 2



Analysis of the Curves of Circular Dichroism.—Measurement of ellipticity was carried out in both the absorption bands and these are found to be opposite in sign. From the ellipticity, the circular dichroism has been calculated by the relation

$$(\epsilon_l - \epsilon_r) = \frac{4 \times 0.4343 \times \phi}{57.296 \times l}$$

where ϕ is the ellipticity expressed in degrees and l is the length of the solution in centimetre. The observed values of $(\epsilon_l - \epsilon_r)$ are given in Table II against the respective frequencies. The experimental curve of circular dichroism for both the bands is represented in Fig. 2. The dissymmetry factor $g = (\epsilon_l - \epsilon_r)/\epsilon$ is also tabulated in Table II. The circular dichroism curves have been represented by our empirical equations (*loc. cit.*) and the calculated values of $(\epsilon_l - \epsilon_r)$ are given in Table II.

Analysis of the Curve of Rotatory Dispersion.—The experimental data for the measurement of the rotatory dispersion are given in Table III. These observed rotations $[\alpha]$ for each wave-length are the algebraic sum of all the partial rotations due to different optically active absorption bands in the visible and ultraviolet regions. These observed values of rotations are represented graphically as curve 1 in Fig. 3.

The following equations have been used to analyse the curve of rotatory dispersion:

- (a) Equation of Kuhn and Braun (*loc. cit.*) in the form as used by the author

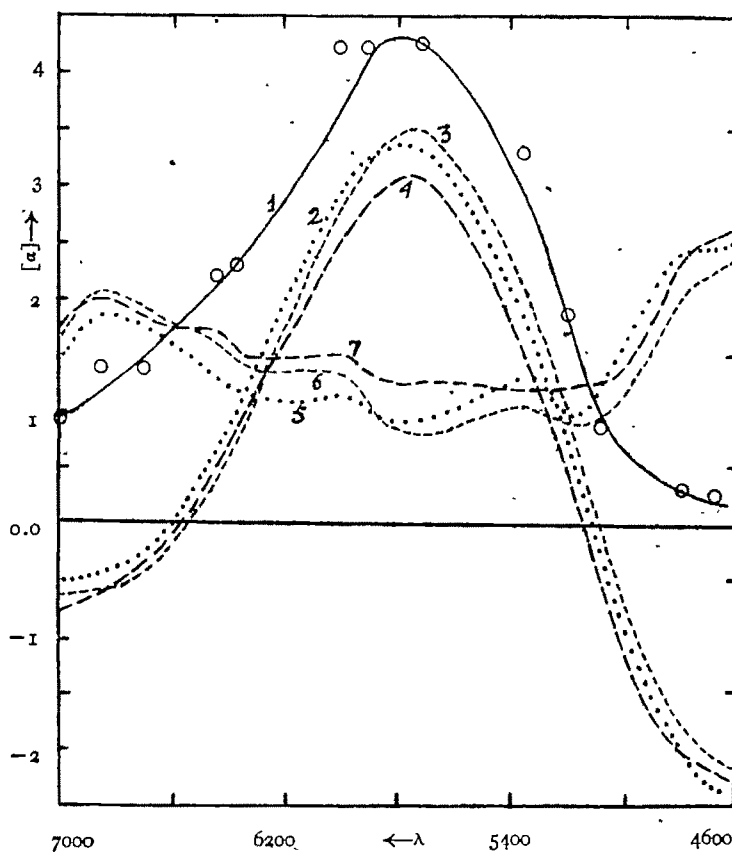


FIG. 3

Rotatory dispersion of sodium vanadyl *d*-tartrate

1. Experimental curve.
2. Theoretical curve calculated from the equation of Kuhn and Braun.
3. - - - - - Theoretical curve calculated from the equation of Lowry and Hudson.
4. — — — — Theoretical curve calculated from our equation
5. Difference curve (curve 1 minus curve 2).
6. - - - - - Difference curve (curve 1 minus curve 3).
7. — — — — Difference curve (curve 1 minus curve 4).

(*J. Indian Chem. Soc.*, 1947, **25**, 461). The values of $(\epsilon_l - \epsilon_r)_{\max}$, ν_0 and θ for both the curves of circular dichroism are already given in Table II. The rotatory contributions at different wave-lengths for each of the absorption bands have been calculated separately. The algebraic sum of the calculated partial rotations $[\alpha]_1$ and $[\alpha]_2$ for different wave-lengths of the two optically active absorption bands in the visible region and the difference between $[\alpha]$ and $[\alpha]_1 + [\alpha]_2$ are given in Table III. This difference evidently represents the residual rotations due to absorption bands in the ultraviolet region. The algebraic sum of the calculated partial rotations and also the residual rotation are represented graphically as curves 2 and 5 in Fig. 3. The difference curve 5 should be normal, i.e., the rotation should increase progressively with decreasing wave-lengths in the region of the first and second absorption bands but

(c) Equation of Kar (*J. Indian Chem. Soc.*, 1947, **24**, 461). The algebraic sum of the calculated partial rotations and the difference between the observed rotation and this sum are also given in Table III and represented graphically as curves 4 and 7 in Fig. 3. The difference curve 7 shows that the loop, which has to be eliminated, shows a sign of improvement, though not disappeared, thus indicating that our equation represents the partial rotations of both the bands more accurately than the equation of Kuhn and Braun and of Lowry and Hudson.

The authors wish to express their gratitude to Sir J. C. Ghosh, Prof. S. N. Bose and Mr. S. R. Mukherjee for the kind interest they took in this investigation.

DEPARTMENT OF PHYSICAL CHEMISTRY,
UNIVERSITY OF DACCA.

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SYNTHESIS OF SUBSTITUTED DINITROPHENYL KETONES AND PHENYLACETIC ACIDS. PART IV

BY A. B. SEN AND P. M. BHARGAVA

2:4-Dinitro-6-chlorophenylacetone and 2:4-dinitro-6-chlorophenylacetic acid have been prepared by the ketonic and acid hydrolysis of 2:4-dinitro-6-chlorophenylacetoacetic ester. The ketone has been characterised by preparation of suitable derivatives. The reduction of 2:4 dinitro-6-chlorophenylacetoacetic ester by iron powder and water has also been carried out.

In the previous communications (J. Indian Chem. Soc., 1947, 24, 268, 371; 1948, 28, 282), 1-chloro-2:4-dinitro-6-bromobenzene, 1-chloro-2:6-dinitro-4-bromobenzene and 1-chloro-2:4-dinitro-6-iodobenzene have been condensed with acetoacetic ester and malonic ester, yielding the corresponding substituted acetoacetic and malonic esters, which on ketonic and acid hydrolysis yielded the corresponding phenylacetones and phenylacetic acids respectively. In this paper this reaction has been extended to 1:6-dichloro-2:4-dinitrobenzene. 2:4-Dinitro-6-chlorophenylacetoacetic ester has also been reduced with iron powder and water to an indole derivative.

EXPERIMENTAL

2:4-Dinitro-6-chlorophenol was obtained previously by the nitration of *o*-chlorophenol (Muller, *Arch. Phar.*, 1875, 203, 111, 120; Faust and Muller, *Annalen*, 1876, 173, 312, etc.). Exact experimental details being not available, it was obtained by the present authors in the following way.

o-Chlorophenol (15 g.) was added dropwise to an ice cooled mixture of nitric acid (conc., 51 c.c.) and water (17.1 c.c.) under continuous mechanical stirring. It was then heated with a low flame on a wire gauze till fumes of nitric acid ceased to be evolved. The mixture was then cooled, diluted with water and filtered. On recrystallisation from dilute alcohol, the phenol was obtained as a pale yellow crystalline substance, m.p. 113°, yield 24 g. (94.1% of theory).

2:4-Dinitro-6-chlorophenylacetoacetic Ester.—The sodium derivative of acetoacetic ester was prepared from acetoacetic ester (18 g.) and sodium (3 g.) in 50 c. c. of dry ether in a welded-neck flask fitted with a mechanical stirrer and a reflux condenser. The flask was then cooled in ice and 1:6-dichloro-2:4-dinitrobenzene (14 g.), prepared from 2:4-dinitro-6-chlorophenol by the method of Ullmann and Sane (*Ber.*, 1911, 44, 3731) added. The mixture was stirred in the cold for 2 hours and then refluxed on a water-bath for another 6 hours. Next day it was extracted with 2% caustic soda solution (300 c.c.); the aqueous extract was separated, cooled with ice and then acidified with dilute nitric acid, when a red oil separated. It was left in a refrigerator for 2 days, the supernatant aqueous layer was decanted off, the oil dissolved in cold alcohol, and the alcoholic solution filtered and left over for slow evaporation. After a few days the ester crystallised out in the form of light brown-red plates, m.p. 64°, yield 11.5 g. (59% of theory). (Found: N, 8.61. $C_{12}H_{11}O_7N_2Cl$ requires N, 8.47 per cent).

2:4-Dinitro-6-chlorophenylacetone.—The above ester (4 g.) was dissolved in sulphuric acid (conc., 50 c.c.), and water (24 c.c.) was added to it without cooling with continuous stirring. After the evolution of CO_2 had ceased, the solution was poured on crushed ice and filtered. On recrystallisation of the crude ketone from hot alcohol, it was obtained as colourless crystals, m.p. 99° , yield theoretical. (Found: N, 10.63. $\text{C}_9\text{H}_7\text{O}_5\text{N}_2\text{Cl}$ requires N, 10.48 per cent).

The *phenylhydrazone* of the above ketone was obtained by adding phenylhydrazine (1.5 c.c.) to a solution of the ketone (1 g.) in hot alcohol and refluxing for half an hour. The solution was cooled in ice, diluted with water, left in a refrigerator overnight and then filtered. On recrystallisation from hot alcohol, the phenylhydrazone was obtained as orange-red needles, m.p. 120° , yield 1.2 g. (91.1% of theory). (Found: N, 16.06. $\text{C}_{18}\text{H}_{13}\text{O}_4\text{N}_4\text{Cl}$ requires N, 15.86 per cent).

The *oxime* of the above ketone was obtained by dissolving the ketone (1.5 g.) in hot alcohol, cooling and adding to it hydroxylamine hydrochloride (1.5 g.) followed by a drop of phenolphthalein and then caustic soda solution drop by drop, till the solution was alkaline to phenolphthalein. It was then refluxed for 1 hour, cooled, then poured in 50 c.c. of cold water and left in a refrigerator overnight. The supernatant liquid was decanted, the sticky mass dissolved in alcohol, the alcoholic solution filtered and the filtrate left over for slow evaporation, when fine, orange coloured crystals of the oxime were deposited, m.p. 95° , yield 1.1 g. (69.3% of theory). (Found: N, 15.19. $\text{C}_9\text{H}_8\text{O}_3\text{N}_2\text{Cl}$ requires N, 15.32 per cent).

2:4-Dinitro-6-chlorophenylacetic Acid.—The ester (1 g.) was hydrolysed with 20% alcoholic potash (12 c.c.) to which water (1 c.c.) had been added, on a water-bath for 1 hour. The alcohol was then distilled off, the residue cooled, acidified with dilute hydrochloric acid, allowed to stand in a refrigerator overnight and then filtered. The product was dissolved in hot alcohol, filtered and the filtrate left over for slow evaporation, when the acid crystallised out as a dark brown powder. It does not melt, but decomposes on heating strongly, yield 0.7 g. (88.8% of theory). (Found: N, 10.45. $\text{C}_9\text{H}_5\text{O}_6\text{N}_2\text{Cl}$ requires N, 10.75 per cent).

2-Methyl 3-carboxyethyl-5-iodo-7-aminoindole.—The ester (1.6 g.), iron powder (3 g.), crystallised ferrous sulphate (0.3 g.) and water (10 c.c.) were refluxed for 3 hours and then cooled with stirring in ice. It was then filtered, the residue extracted with boiling alcohol, the extract filtered hot, and the filtrate allowed to evaporate by itself when fine brown needles of the reduction product were obtained, m.p. $126-27^\circ$ (decomp.), yield 0.7 g. (57.3% of theory). (Found: N, 10.74. $\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}_2\text{Cl}$ requires N, 11.09 per cent).

One of the authors (P. M. B.) is indebted to the Lucknow University for award of a research grant.

PRODUCTION OF THE JOSHI EFFECT IN OXYGEN UNDER SILENT ELECTRIC DISCHARGE: PART I. INFLUENCE OF THE EXCITING POTENTIAL AND THE GAS PRESSURE

BY S. R. MOHANTY AND G. S. KAMATH

The Joshi effect, Δi , an instantaneous and reversible photo-variation (usually, diminution) of the discharge current i in gases, has been studied in oxygen in the range 10-500 mm Hg (p) and excited by ozoniser discharges over 0.5 to 6 kilo-volts (V) of 50 cycles frequency. 'Threshold potential' V_m , at which i increases rapidly with V , varies sensibly linearly with p . Well below V_m , Δi is not detected. Above V_m , Δi at constant p first increases with V and then decreases. The relative effect, % Δi , is a maximum near V_m , and diminishes thereafter. The potential distribution in respect of both Δi and % Δi is flat at higher p , which is significant for the pressure-dependence of the mechanism of Δi . The authors' observation under a wide range of conditions of up to 50% current decrease in oxygen under but visible light suggests that the Joshi effect is not a special reaction limited to excited halogens. The generality of results are in accord with Joshi's theory of this phenomenon.

Joshi and Deshmukh (*Nature*, 1941, **147**, 806) and Deshmukh (*J. Indian Chem. Soc.*, 1947, **24**, 211), using special large discharge tubes, intense radiations of short wave-length, and current-sensitive indicators observed the Joshi effect, Δi , in oxygen excited by 'silent discharge'; Δi corresponded to about 4%. This was confirmed by the results of Joshi and Cherian (*Proc. Indian Sci. Cong.*, 1942, Part III, *Chem. Sec.*, Abst. No. 56), and Mohanty and co-workers (*ibid.*, 1947, Part III, *Phys. Sec.*, Abst. Nos. 14, 15; 1948, *Phys. Sec.*, Abst. Nos. 13, 19; *Chem. Sec.*, Abst. Nos. 35, 36). Apart from these preliminary observations, the entire work on this new phenomenon has been confined to halogens, especially chlorine which shows Δi to the largest extent. It was of interest therefore to investigate in some detail its production in oxygen.

EXPERIMENTAL

The apparatus used (Fig. 1) consisted essentially of a discharge vessel formed with two co-axial glass tubes fused together as in a Siemens' ozoniser. This was connected on one hand through taps T_4 and T_5 , a cooling spiral S and tap T_2 to a reservoir R of pure oxygen; and to a mercury manometer M , and Töpler on the other. The whole or any desired part of the apparatus could be connected to the Töpler by manipulation of taps T_1 to T_6 . The entire all-glass assembly was tested for a satisfactory vacuum for at least 48 hours before commencing any given series of experiments. Oxygen was obtained by heating carefully pure potassium permanganate in the hard glass tube, H , plugged with glass-wool. It was dried by leading slowly through a train of tubes containing respectively fused calcium chloride, potassium hydroxide and phosphorus pentoxide. The first lot of the evolved gas was rejected by pumping off with the Töpler through tap T_6 , taps T_1 and T_2 being closed. A given series of Δi observations was commenced after the entire apparatus was washed repeatedly with purified oxygen

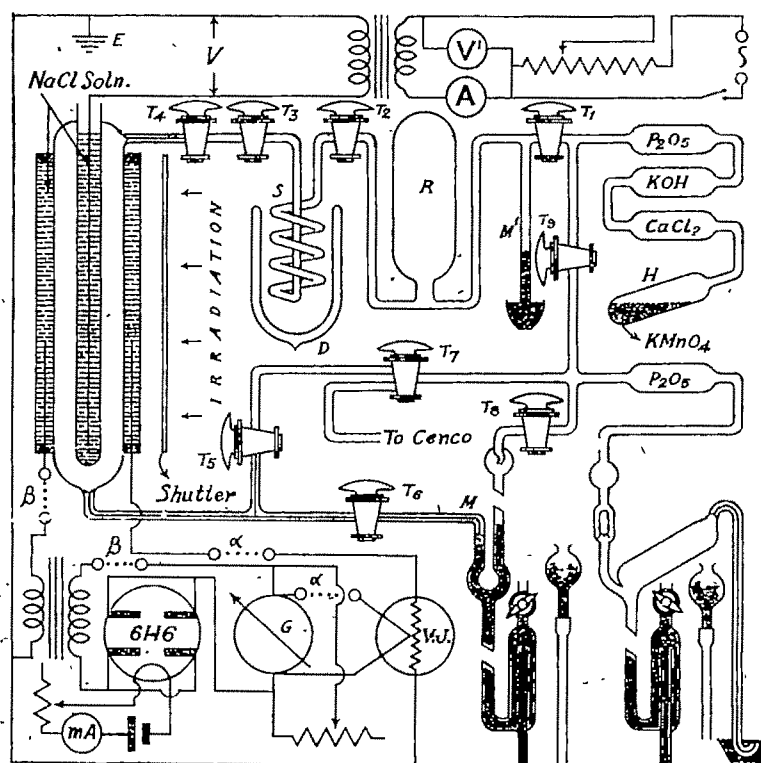
subjected to discharge in the ozoniser and tóplered off. This served to eliminate any traces of adsorbed impurities. Before admitting into the ozoniser at a desired pressure, oxygen from R was first led slowly through the spiral S, cooled by liquid air in the Dewar flask, D. This removed, by freezing out, any condensible impurities in the gas. The pressure of the gas in the ozoniser was observed with the manometer, M. To prevent rise in temperature of the gas in the ozoniser due to heat produced under discharge, water at a temperature within $\pm 1^\circ$ was circulated through a glass jacket (not shown in Fig. 1) surrounding the ozoniser system.

Two ozonisers A and B were used. They had the following dimensions :

	A (Monax glass)	B (Indian soft soda glass)
External diameter of the outer tube in mm	22.5	20.5
Internal " " " "	20	17.5
External " inner " " "	15	14
Internal " " " "	12.5	11
Thickness of the glass wall " "	1.25	1.5
Inter-electrode distance "	2.5	1.75
Length of the electrode space "	965	432

FIG. 1

Production of the Joshi effect in oxygen



The electrical connections are shown in Fig. 1. A single phase alternating current of 50 cycles frequency was obtained from a 1 kW rotary converter worked off 220 volt, D. C. mains. Its output was fed to the primaries of a high-tension transformer. The primary current and voltage were observed by an ammeter, A and a voltmeter, V' respectively. The ozoniser terminals, represented by a 10% solution of sodium chloride inside the inner tube and in the bath surrounding the outer tube of the ozoniser, were connected to the secondaries of the high-tension transformer. The P. D. across the secondaries V applied to the ozoniser was varied, and kept constant within 1% at a desired value, by hand regulation of the primary voltage with the potentiometric arrangement shown (Fig. 1).

The discharge current i flowing through the ozoniser A was detected by a mirror galvanometer G, actuated by a Cambridge vacuo-junction V. J., the connections being through α , α (Fig. 1); that flowing through the ozoniser B was passed through the primaries of a Bell type 3:1, step-up iron-core transformer by making connections through β , β (α , α having been disconnected). The secondaries of the transformer were connected to the plates and the cathodes of a (RCA) 6H6 double diode through G which was suitably shunted. The filament of the valve was heated by a current of 270 mA obtained from a 6 volt storage cell.

The source of irradiation consisted of a battery of 200 watt (glass) bulbs run at 200 volts. The current in the dark i_b was noted with the source of light on, and the shutter in position. On moving the shutter, the discharge vessel was flooded with light, and the current diminished immediately to i_L . On shutting off the light, it increased similarly to its original value, i_b .

Ozoniser A, filled with purified oxygen at various pressures in the range of 10 to 250 mm. Hg, was subjected to different alternating potentials V varied over 0.5–4 kV (r. m. s.). In Table I, which represents but one typical series of results with this ozoniser, are shown the discharge current in dark i_b , that under irradiation i_L , the net Joshi effect $\Delta i = i_b - i_L$, and the proportional effect expressed as a percentage, i.e., $100\Delta i/i_b$; since vacuo-junction was the detector, the current values are in square root of the corresponding galvanometer deflections. Table II represents another group of typical data with ozoniser B in the pressure range of 50 to 500 mm. and excited by 0.5 to 6 kV; the current values are in galvanometer deflections, the A. C. indicator being a diode. In Figs. 2 and 3 are shown the V- i characteristics for oxygen gas in the ozonisers A and B respectively for different pressures, in dark (continuous curves), and under irradiation (discontinuous curves). These curves show the essence of the phenomenon, viz., that i produced due to various applied V diminishes as a result of irradiation. The continuous curves at the bottom of Figs. 2 and 3 illustrate the variation of the net effect Δi with V; curves shown by dots and dashes show the corresponding variation of $\% \Delta i$. In Fig. 4 are plotted the 'threshold potentials' V_m (*vide infra*) for oxygen in ozoniser B at various gas pressures.

TABLE I

Potential variation of the Joshi effect in oxygen at different gas pressures with vacuo-junction detection.

(Ozoniser A)

Temp. = 19°—21°. Frequency of A. C. supply = 50 cyc./sec. Source of irradiation = Three 200 watt (glass) bulbs run at 200 volts, and 22 cm. from A.

Pressure of oxygen in mm											
	10.	21. V=0.67.	31.	10.	21. V=0.8.	31.	43.	10.	21. V=0.93.	31.	43.
i_D	4.12	3.74	2.45	3.61	5.39	5.1	3.74	3.46	5.2	6.25	5.66
i_L	2.24	2.45	1.58	2.24	3.61	3.74	2.45	2.65	3.87	4.58	4.00
Δi	1.88	1.29	0.87	1.37	1.78	1.36	1.29	0.81	1.33	1.67	1.66
% Δi	45.6	34.5	35.5	38	33.0	26.7	34.5	23.4	25.6	26.7	29.3

Pressure of oxygen in mm.								
	10.	21. V=1.07	31.	43.	10.	21. V=1.2	31.	43.
i_D	3.61	5.39	6.93	6.33	3.81	5.57	7.35	6.78
i_L	3.00	4.24	5.1	4.8	3.46	4.58	5.57	5.29
Δi	0.61	1.15	1.83	1.53	0.35	0.99	1.78	1.49
% Δi	16.9	21.3	26.4	24.2	9.2	17.8	24.2	22

Pressure of oxygen in mm.										
V.	10.	21.	31.	43.	50.	100.	150.	200.	250.	
1.33	i_D	4.06	5.57	7.62	7.21	7.55	4.8			
	i_L	3.81	4.9	5.29	5.83	5.92	3.74			
	Δi	0.25	0.67	1.70	1.38	1.63	1.06			
	% Δi	6.2	12.0	22.3	19.1	21.6	22.1			
1.47	i_D	4.47	5.92	8.06	7.94	8.06	5.29			
	i_L	4.24	5.24	6.29	6.33	6.48	4.24			
	Δi	0.23	0.68	1.77	1.61	1.58	1.05			
	% Δi	5.1	11.5	22	20.3	19.6	19.9			
1.6	i_D	4.85	6.25	8.43	8.38	8.49	6.25			
	i_L	4.69	5.70	6.78	6.75	7.00	5.1			
	Δi	0.16	0.55	1.65	1.59	1.49	1.15			
	% Δi	3.3	8.8	19.6	19.1	17.6	18.4			
1.73	i_D	5.29	6.63	8.37	8.89	8.78	7.00			
	i_L	5.15	5.92	7.00	7.21	7.55	6.16			
	Δi	0.14	0.71	1.37	1.68	1.23	0.84			
	% Δi	2.6	10.7	16.4	18.9	14.0	12.9			
1.87	i_D	5.61	6.93	8.83	9.27	9.11	8.12			
	i_L	5.48	6.33	7.48	7.81	7.94	7.00			
	Δi	0.13	0.60	1.35	1.46	1.17	1.12			
	% Δi	2.3	8.7	15.3	15.8	12.8	13.8			
2	i_D	6.08	7.18	8.92	9.75	9.38	8.60	6.25	3.32	
	i_L	6.00	6.71	7.94	8.25	8.25	7.68	5.48	3.00	
	Δi	0.08	0.47	0.98	1.50	1.13	0.92	0.77	0.32	
	% Δi	1.3	6.5	11	15.4	12.1	10.7	12.3	9.6	
2.13	i_D	6.56	7.42	9.27	10.15	9.7	9.11	7.42	4.58	3.74
	i_L	6.48	6.86	8.00	8.69	8.66	8.25	6.48	4.12	3.46
	Δi	0.08	0.56	1.27	1.45	1.04	0.86	0.94	0.46	0.28
	% Δi	1.2	7.5	13.7	14.4	10.7	9.4	12.7	10.0	7.5
2.27	i_D	7.07	8.25	9.43	10.58	9.95	9.7	8.49	5.2	4.36
	i_L	7.07	7.94	8.72	9.17	9.06	8.89	7.75	4.69	4.06
	Δi	—	0.31	0.71	1.41	0.89	0.81	0.74	0.51	0.30
	% Δi	—	3.8	7.5	13.3	8.9	8.4	8.7	9.8	6.9

TABLE I (contd.)

		Pressure of oxygen in mm.						
V.		31.	43.	50.	100.	150.	200.	250.
2.4	t_D	9.64	10.86	10.30	10.20	9.43	5.83	5.00
	t_L	9.08	9.59	9.43	9.49	8.66	5.48	4.69
	Δt	0.56	1.27	0.87	0.71	0.77	0.35	0.31
	$\% \Delta t$	5.8	11.7	8.4	7	8.2	6.0	6.2
2.53	t_D	10.1	11.40	10.73	10.86	10.24	6.86	5.66
	t_L	9.59	10.15	10.00	10.20	9.43	6.33	5.29
	Δt	0.51	1.25	0.73	0.66	0.81	0.53	0.37
	$\% \Delta t$	5.1	11	6.8	6.1	7.9	7.7	6.5
2.67	t_D	10.1	11.69	11.05	11.40	10.93	7.75	6.40
	t_L	9.8	10.52	10.40	10.77	10.2	7.00	6.00
	Δt	0.3	1.17	0.65	0.63	0.73	0.75	0.40
	$\% \Delta t$	3	10.0	5.9	5.5	6.7	9.7	6.3
2.8	t_D	10.4	12.04	11.40	11.96	11.64	8.54	7.17
	t_L	10.2	11.03	10.77	11.36	10.91	8.00	6.71
	Δt	0.2	1.01	0.63	0.60	0.73	0.54	0.43
	$\% \Delta t$	1.9	8.4	5.5	5.0	6.3	6.3	6.0

Pressure of oxygen in mm.

	150.	200.	250.	150.	200.	250.	150.	200.	250.	150.	200.	250.
	V=2.93			V=3.07			V=3.2			V=3.33		
t_D	12.21	9.43	8.06	12.84	10.15	8.89	13.35	10.58	9.7	13.90	10.95	10.49
t_L	11.49	8.89	7.62	12.17	9.54	8.43	12.69	9.8	9.17	13.19	10.58	10.00
Δt	0.72	0.54	0.44	0.67	0.61	0.46	0.66	0.78	0.53	0.71	0.37	0.49
$\% \Delta t$	5.9	5.7	5.5	5.2	6.0	5.2	4.9	7.4	5.5	5.1	3.4	4.7

TABLE II

Potential variation of the Joshi effect in oxygen at different gas pressures, with diode detection.

(Ozoniser B)

Temp.=27°-29°. Frequency of A. C. supply =50 cyc./sec. Source of irradiation =Two 200 watt (glass) bulbs run at 200 volts, and 15 cm. from B.

Pressure of oxygen in mm.

	52.	52.	52.	52.	101.	52.	101.
	V=0.67.	V=0.8.	V=0.93.		V=1.07.		V=1.2.
t_D	3	20	89		113	1	124
t_L	3	13	51		67	1	77
Δt	—	7	38		46	—	47
$\% \Delta t$	—	35.0	42.7		40.7	—	37.9

Pressure of oxygen in mm.

	52.	101.	148.	52.	101.	148.	52.	101.	148.	52.	101.	148.
	V=1.33.			V=1.47.			V=1.6.			V=1.73.		
t_D	142	97	2	159	120	8	174	138	32	189	148	119
t_L	93	61	2	105	75	6	118	90	20	130	100	71
Δt	49	36	—	54	45	2	56	48	12	59	48	39
$\% \Delta t$	34.5	37.1	—	34.0	37.5	25.0	32.2	34.8	37.5	31.2	32.4	35.5

Pressure of oxygen in mm.

	52.	101.	148.	250.	52.	101.	148.	250.
	V=1.87.				V=2.			
t_D	203	161	144	2	217	171	167	8
t_L	139	108	91	2	153	117	105	5
Δt	64	53	53	—	64	54	62	3
$\% \Delta t$	31.5	32.9	36.8	—	29.5	31.6	37.1	37.5

TABLE II (contd.)

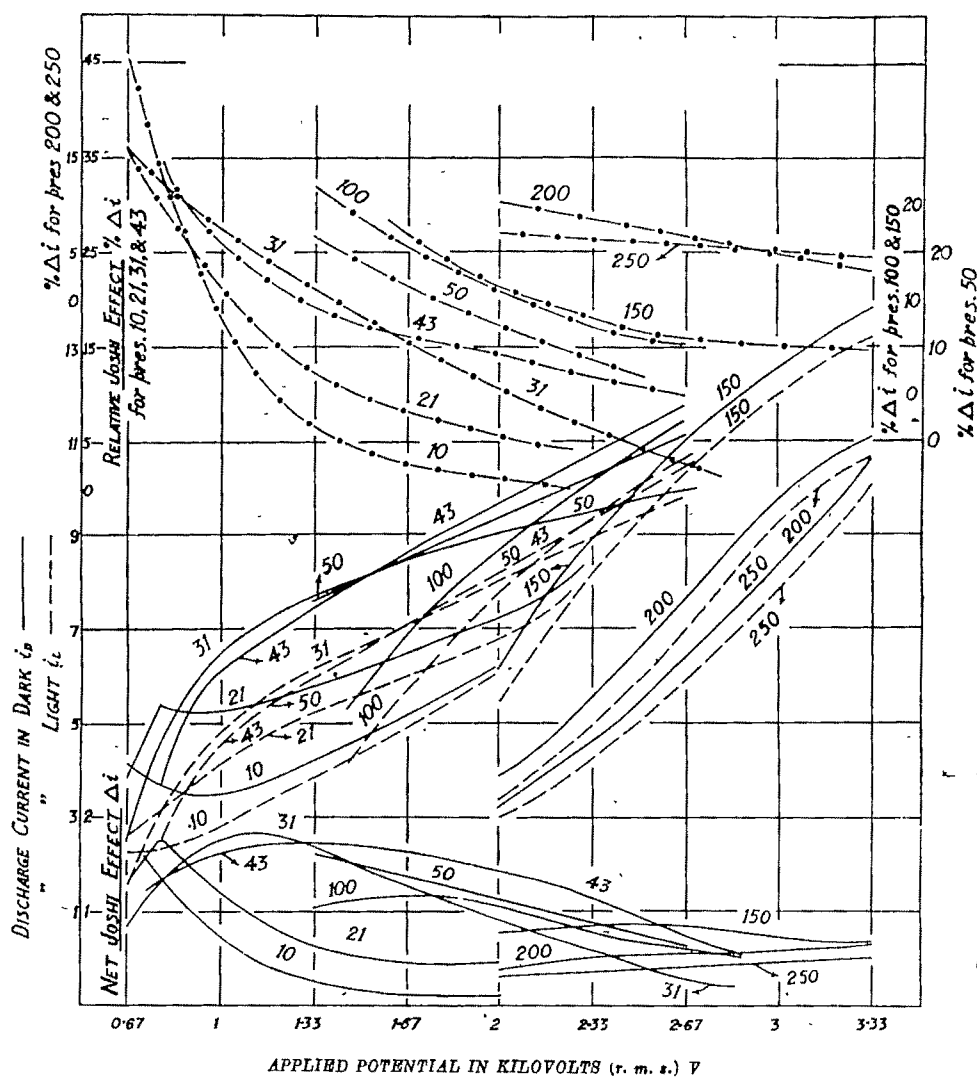
		Pressure of oxygen in mm.					
V.		52.	101.	148.	250.	346.	456.
2.13	i_D	235	186	181	16	5	
	i_L	165	131	118	10	5	
	Δi	70	55	63	6	—	
	% Δi	29.8	29.6	34.8	37.5	—	
2.27	i_D	245	203	192	35	8	
	i_L	175	143	127	20	6	
	Δi	70	60	65	15	2	
	% Δi	28.6	29.6	33.6	42.9	25.0	
2.4	i_D	264	214	204	72	19	
	i_L	188	152	136	42	12	
	Δi	76	62	68	30	7	
	% Δi	28.8	29	33.3	41.7	36.8	
2.53	i_D	274	230	221	162	27	
	i_L	198	168	152	99	17	
	Δi	76	62	69	63	10	
	% Δi	27.5	27	31.2	38.9	37	
2.67	i_D	290	245	235	195	39	5
	i_L	212	179	163	124	24	5
	Δi	78	66	72	71	15	—
	% Δi	26.9	27	30.6	36.4	38.5	—
2.93	i_D	314	268	264	242	78	12
	i_L	233	201	186	162	43	9
	Δi	81	67	78	80	35	3
	% Δi	25.8	25	29.5	33.6	44.9	25
3.2	i_D	335	289	283	264	172	26
	i_L	253	219	203	177	105	17
	Δi	82	70	80	87	67	9
	% Δi	24.5	24.2	28.3	32.9	39	34.7
3.47	i_D	355	309	303	302	224	60
	i_L	270	239	221	209	146	32
	Δi	85	70	82	93	78	28
	% Δi	23.9	22.7	27.1	30.8	34.8	46.7
3.73	i_D	373	324	320	328	274	155
	i_L	285	251	237	234	185	87
	Δi	88	73	83	94	89	68
	% Δi	23.6	22.5	26.0	28.7	32.5	43.9
4	i_D	390	341	337	359	316	204
	i_L	300	265	251	261	221	124
	Δi	90	76	86	98	95	80
	% Δi	23.1	22.3	25.5	27.3	30.1	39.2
4.27	i_D	406	357	352	383	349	247
	i_L	313	282	264	281	248	150
	Δi	93	75	88	102	101	97
	% Δi	22.9	21.0	25.0	26.6	28.9	39.3
4.53	i_D	420	372	368	408	376	286
	i_L	325	295	279	300	275	182
	Δi	95	77	89	108	101	104
	% Δi	22.6	20.7	24.2	26.5	26.9	36.4
4.67	i_D	428	381	377	418		
	i_L	330	303	286	308		
	Δi	98	78	91	110		
	% Δi	22.9	20.5	24.1	26.3		
		346	456	346	456.	346.	456.
		V=4.8		V=5.07		V=5.33	
	i_D	439	345	474	371	411	316
	i_L	330	235	360	255	308	206
	Δi	109	110	114	116	103	110
	% Δi	24.8	31.9	24.1	31.3	25.1	34.8

DISCUSSION

That the minimum 'threshold potential' V_m is an important determinant of the rate and nature of a chemical or quasi-chemical change in gaseous systems under electrical

FIG. 2

Potential variation of the Joshi effect in oxygen at different gas pressures, with vacuo-junction detection (ozoniser A).

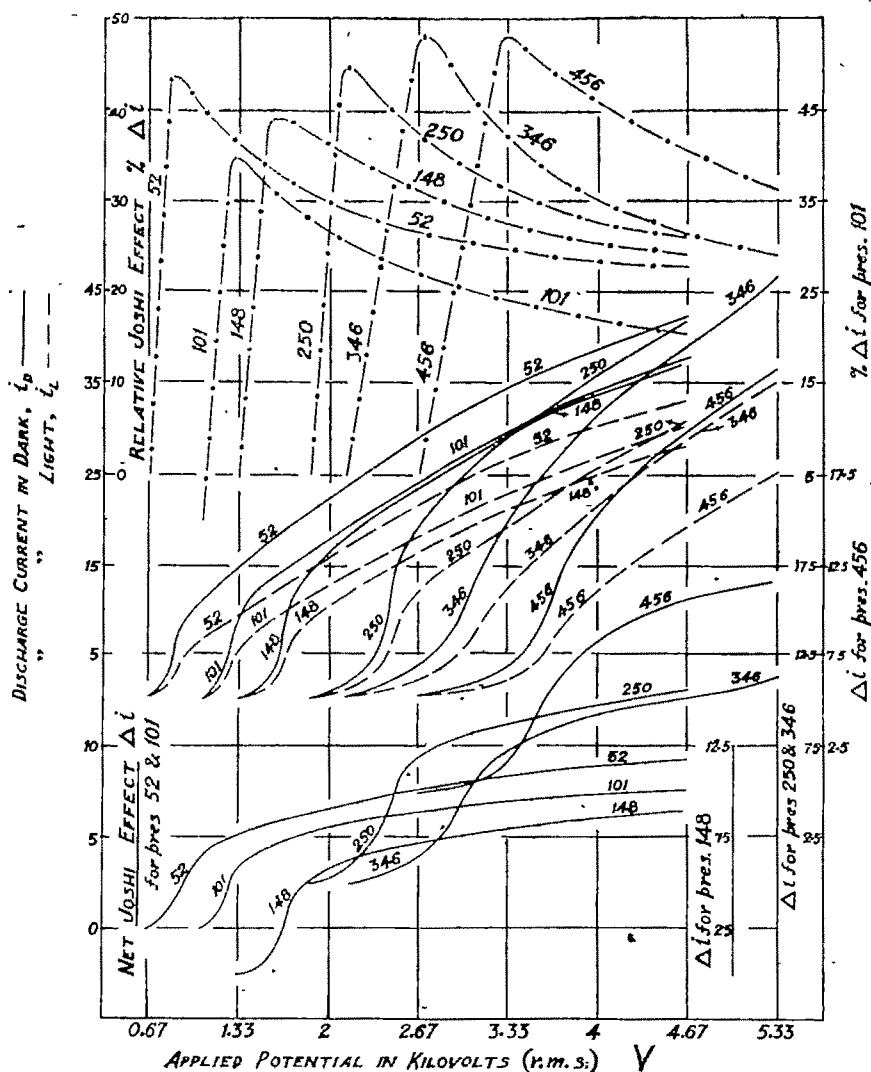


discharge, has been observed by Joshi (*Trans. Faraday Soc.*, 1929, **25**, 118, 137; *Proc. Indian Sci. Cong.*, 1931, Part III, Chem. Sec., Abst No. 63; *Curr. Sci.*, 1939, **8**, 548; 1946, **15**, 281; *Proc. Ind. Acad. Sci.*, 1945, **22A**, 389). This V_m may be related simply to the corresponding Paschen potential, especially in elementary gases. It is marked by a sudden increase in the current through, and the wattage dissipated

in, the system. From the $V-i$ characteristics in Fig. 3 (cf. Table II) it is seen that at first, i is but small and increases slowly with V . The breakdown of the gas as a dielectric is well marked above V_m , as shown by the noticeably large current rise for a given voltage increase. Thus *e. g.*, i_b for ozoniser A filled with oxygen at 43 mm. is undetected at 0.67 kV (Table I). Above this potential, it rises rapidly, to 3.74 at 0.8 kV, and 5.66 at 0.93 kV. For ozoniser B at 346 mm. (Table II), i_b is 5 at 2.13 kV, increases slowly to 78 at 2.93 kV and thence rapidly to 172 at 3.2 kV. The 'threshold potential' V_m for oxygen in ozoniser B, obtained by extrapolation of the corresponding $V-i_b$ characteristic curves in Fig. 3, is sensibly a linear function of the gas pressure p

FIG. 3

Potential variation of the Joshi effect in oxygen at different gas pressures, with diode detection (ozoniser B).



over a fairly wide range (Fig. 4). This also obtains with the Paschen potential. The increase of V_m , as of the Paschen potential, with p results from the increased number of encounters with molecules of an ion or/and electron in the inter-electrode space.

It is a general finding of Joshi (*Proc. Ind. Acad. Sci.*, 1945, **22A**, 389) that well below V_m , when the conduction is mainly capacitative, Δi does not occur despite the use of intense and even short-wave radiations and large displacement currents obtained; say, with high frequencies input to the system (Joshi and Lad, *ibid.*, 1945, **22A**, 293). Furthermore, whilst $\% \Delta i$ is maximum near V_m and decreases with V , the net effect Δi increases initially and decreases thereafter. As will be seen from Fig. 3 (*cf.* also Table II), apparently Δi in oxygen sets in below V_m as defined above. It rises near this potential followed by a slow rise with V afterwards (Figs. 2 and 3. *cf.* Tables I and II); at still higher V , however, it is reduced (Fig. 2. *cf.* Table I). Thus *e. g.*, V_m for $pO_2 = 250$ mm. in ozoniser B is 2.23 kV. The effect at this pressure is just detectable at 2 kV (Table II). Δi increases rapidly from 3 at 2 kV to 71 at 2.67 kV and slowly afterwards to 110 at 4.67 kV. As suggested by the Δi — V curves in Fig. 2, it is important to emphasise that the increase in Δi with V is distributed over a wider range of V at higher than at lower gas pressures. Thus, whilst at $pO_2 = 21$ mm., Δi reaches a maximum (of 1.78) at 0.8 kV and decreases thereafter, at 250 mm. it is still increasing at 3.33 kV. The subsequent fall in Δi with V is not noticeable in Fig. 3 up to the maximum potential applied, viz., 4.67 kV for pressures 52, 101, 148 and 250 mm., and 5.33 kV at 346 and 456 mm.

The relative effect $\% \Delta i$ is but small below V_m , increases rapidly with V and attains a maximum near V_m (Fig. 3). Above this potential it decreases (Figs. 2 and 3). Thus *e. g.*, V_m for $pO_2 = 346$ mm. in ozoniser B is 2.73 kV. The relative effect, $\% \Delta i$ increases from 25.0 at 2.27 kV to 44.9 at 2.93 kV and decreases with further increase in V to 24.1 at 5.33 kV (Table II). As will be evident from the $\% \Delta i$ — V curves in Figs. 2 and 3, the variation with V of $\% \Delta i$ is more gradual at higher than at lower gas pressures. The comparatively flat distribution over a given voltage range, both of Δi and $\% \Delta i$, especially at higher gas pressures, as shown by the corresponding curves in Figs. 2 and 3, has significance for a general theory of this Δi phenomenon and its dependence on the gas pressure.

It is instructive to consider Δi values at constant i_b for various gas pressures as read off from the ordinates of the i_b and i_c curves in Figs. 2 and 3. That when so considered Δi for oxygen in ozoniser A increases with p up to a limiting pressure, viz., 43 mm. and then decreases is evident from results (deduced from V — i curves in Fig. 2) cited herein under.

$pO_2(\text{mm.})$ $i_b = 8$	10	21	31	43	50	100	150	200	250
Δi	0.0	0.35	1.5	1.6	1.5	1.05	0.8	0.6	0.45
$\% \Delta i$	0.0	4.4	18.8	20.0	18.8	13.1	10.0	7.5	5.6

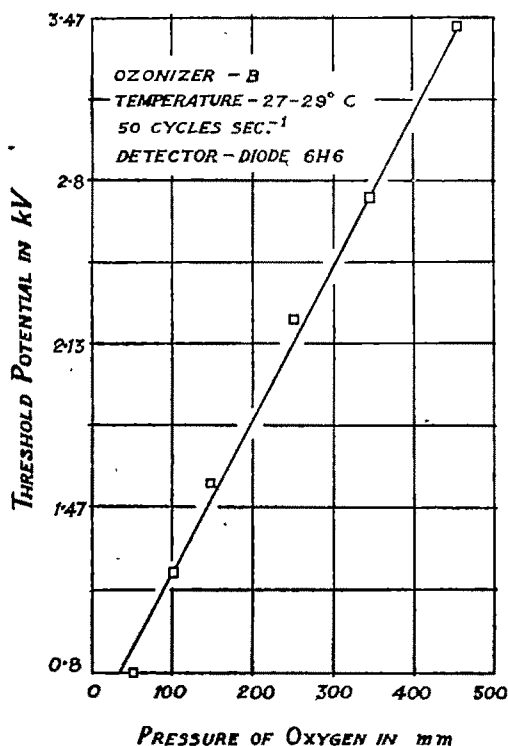
In the case of ozoniser B, which had a greater electrode separation and a consequent concentration of the field near the surface of the inner electrode, Δi at constant i_b continues to increase with p up to even the largest value used, viz., 456 mm. This is seen from the following results obtained from V — i curves in Fig. 3.

pO_2 (mm.)	54	101	148	250	346	456
$i_0 = 200$						
Δi	62	58	65	71	73	83
% Δi	31	29	32.5	35.5	36.5	41.5

The above difference in the pressure influence of Δi and % Δi in ozonisers A and B might also originate from the difference in the nature of the detector employed.

FIG. 4

Variation with gas pressure of threshold potential V_m of oxygen.



Joshi (*Proc. Indian Sci. Cong.*, 1946, Part III, *Phys. Sec.*, Abst No. 26; 1947, *Phys. Sec.*, Abst.; *Curr. Sci.*, 1946, **15**, 281; 1947, **16**, 19) has suggested the formation, under discharge, of an adsorption-like ionic+molecular electrode layer as primary to Δi . Photo-electrons emitted from this boundary layer are captured by the electronegative elements in the discharge space forming slow moving negative ions which reduce i by a space charge effect. The electron affinity of the oxygen atom is about 3.80 e. v. (as compared with that of fluorine 3.94, chlorine 3.70, bromine 3.54, and iodine 3.22) (Glockler, *Phys. Rev.*, 1934, **45**, 111); that of the oxygen molecule is 2.7 (Weiss, *Trans. Faraday Soc.*, 1935, **81**, 966). The appreciably high Δi observed in oxygen is therefore to be anticipated. The probability of electron capture depends upon p/E , where p is the gas pressure and E , the applied field. Increase of Δi with p and decrease with V follow, as observed.

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DEPARTMENT OF CHEMISTRY,
BENARES HINDU UNIVERSITY

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ELECTROLYSIS OF MAGNESIUM SULPHATE IN THE PRESENCE OF SULPHURIC ACID

BY DUSHYANT NARASINGASA SOLANKI AND PIDAPARTHI SURYANARAYANA SASTRY

A study has been made of the electrolysis of aqueous $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in the presence of varying proportions of H_2SO_4 . The influence on the production of persulphate of the following factors has been investigated; composition of the electrolyte, inter-electrode distance, current density at the anode and the cathode, temperature, duration of electrolysis, addition agents and cathode material. Data are also given for the optimum conditions for the production of the persalt. High yields of persulphate under studied conditions are attributed to the absence of Caro's acid.

The probable mechanism of the formation of magnesium persulphate is also indicated.

Persulphates and hydrogen peroxide on account of their industrial importance form a subject of great interest. The electrolysis of sulphuric acid gives perdisulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$ (Marshall's acid), which hydrolyses into permonosulphuric acid, H_2SO_5 (Caro's acid), and subsequently into hydrogen peroxide and sulphuric acid. This process, though simple, is not advantageous due to the rapid falling off of the current efficiency (C. E.) with the prolongation of electrolysis as Marshall's acid, and more especially Caro's acid, are comparatively unstable than the persulphates. Müller and Schellhaas (*Z. Electrochem.*, 1907, **13**, 257; 1908, **14**, 121) have shown that in the case of electrolysis of sulphuric acid, the C. E. decreases rapidly and falls even to zero, the rate of formation of Marshall's acid being equal to the rate of decomposition of Caro's acid. The state at which the total amount of peracids remains constant is known as "steady state". It was thought that this difficulty of comparative instability of Marshall's acid, and particularly of Caro's acid, might be overcome by employing MgSO_4 in H_2SO_4 medium as the starting material. From magnesium persulphate hydrogen peroxide can be prepared by its decomposition with H_2SO_4 and hydrolysis under suitable conditions and subsequent distillation under reduced pressure.

L. Li and K. Pei (*Contn. Chem. Nat. Acad., Peiping*, 1935, **2**, 1-20) have shown that in the case of the electrolytic preparation of magnesium persulphate an anodic current density of 70 amp./dm². gives the optimum yield. Work has been in progress in the Electrochemical Laboratories of the Benares Hindu University for some considerable time on the electro-preparation of hydrogen peroxide from H_2SO_4 (Solanki and Sheshadri, *Proc. Ind. Sci. Cong.*, 1942, Part III, p. 43) and from Na_2SO_4 in the presence of sulphuric acid (Joshi, Solanki and Kamath, *Proc. Ind. Acad. Sci.*, 1946, **24A**, 305). The present investigation is in continuation of this line of research and an attempt has been made to find the suitability of MgSO_4 as the starting material. The influence of the various factors, such as the bath composition, temperature of electrolysis on the C. E. of the persulphate formation has been fully investigated and the optimum conditions established.

EXPERIMENTAL

The electrolytic cell consisted of a cylindrical glass jar 10" × 4", closed with a rubber stopper, through which two glass tubes supporting platinum electrodes, a thermometer

and an exit tube for the escape of gases were passed. Current was tapped from the mains and was regulated by a rheostat and lamp resistance. The current was recorded by a precision ammeter arranged in series and P. D. of the cell by a voltmeter connected across the two electrodes. The temperature of the electrolytic cell was kept constant at the desired value (usually 10°); 50 c.c. of the solution were taken for electrolysis each time. Usually a current of one ampere was passed for half an hour. After the electrolysis the cell was gently shaken to make the solution uniform and 5 c.c. of the electrolyte were estimated for total active oxygen by the familiar $\text{FeSO}_4\text{-KMnO}_4$ method in an atmosphere of CO_2 with the usual precautions (Treadwell and Hall, "Analytical Chemistry", Vol. II. 7th ed., John Wiley & Sons, New York, 1930, p. 535).

The influence on the C. E. for the persulphate formation of the following factors was studied :

- (1) Conc. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in neutral solutions.
- (2) Conc. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in H_2SO_4 solution (25 g./100 c.c.).
- (3) Conc. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in H_2SO_4 solution (60 g./100 c.c.).
- (4) Conc. of H_2SO_4 along with $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ soln. (45 g./100 c.c.).
- (5) Anodic current density.
- (6) Cathodic current density.
- (7) Inter-electrode distance.
- (8) Use of diaphragm.
- (9) Duration of electrolysis.
- (10) Temperature of electrolysis.
- (11) Addition agents.
- (12) Cathode material.

The results obtained are shown in Tables I to XII and graphically in curves I to IV in Figure 1.

TABLE I

Influence of concentration of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ on current efficiency.

Anodic current density = 60.6 amp/dm². Current passed = 1 amp. Cathodic current density = 29.3 amp./dm². Duration of electrolysis = 30 mins. Vol. of electrolyte = 50.0 c.c. Inter-electrode distance = 3.1 cm. Temp. = 10° .

Diaphragm not used.

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 c.c. soln.	P. D.	Active O_2 in 5 c.c. of electrolyte soln (in c.c. of $\text{N}/20\text{-KMnO}_4$)	C. E.	Active O_2 per K. W. H.
10 g.	4.0 volts	0	0%	0 g.
30	4.1	0	0	0
50	4.2	0	0	0
70	4.3	8	2.2	2

TABLE II

Influence of conc. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in H_2SO_4 soln. (25 g./100 c.c. soln.) on current efficiency.

Conditions, same as in Table I.

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 c.c. soln.	P. D.	Active O_2 in 5 c.c. of electrolyte soln. (in c.c. of $\text{N}/20\text{-KMnO}_4$)	C. E.	Active O_2 per K. W. H.
20 g.	4.6 volts	41	11.0%	7.13 g.
30	4.6	46	12.2	8.00
40	4.7	68	18.2	11.57
45	4.8	71	19.1	11.83
50	4.8	71	19.1	11.83

TABLE III

Influence of conc. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in H_2SO_4 medium (60 g./100 c.c. soln.) on current efficiency.

Conditions, same as in Table I.

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 c.c. soln.	P. D.	Active O_2 in 5 c.c. of electrolyte soln. (in c.c. of $\text{N}/20\text{-KMnO}_4$)	C. E.	Active O_2 per K. W. H.
20 g.	4.6 volts	20.5	55.0%	35.65 g.
30	5.3	23.4	62.7	35.32
40	5.8	24.2	64.8	33.38
45	6.3	25.0	67.0	31.76
50	6.4	25.4	68.1	31.75

TABLE IV

Influence of conc. of H_2SO_4 on current efficiency.

Conc. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 45$ g./100 c.c. of soln. Other conditions, as in Table I.

H_2SO_4 in 100 c.c. of soln.	P. D.	Active O_2 in 5 c.c. of electrolyte soln. (in c.c. of $\text{N}/20\text{-KMnO}_4$)	C. E.	Active O_2 per K. W. H.
20 g.	5.2 volts	5.4	14.5%	8.31 g.
25	5.4	12.9	19.1	18.11
40	5.6	16.6	44.5	23.71
60	6.3	25.0	67.0	31.76
65	6.3	25.0	67.0	31.76
70	7.0	24.5	65.7	28.00

TABLE V

Influence of anodic current density on C. E.

Composition of electrolyte used = 45 g. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; 60 g. of H_2SO_4 (in 100 c.c. of soln). Current varied as indicated in the first column.

Other conditions, same as in Table I (except anodic C. D.).

Current passed.	Anodic C. D. (amps./dm ²).	P. D.	Active O ₂ in 5 c.c. of electrolyte soln. (in c.c. of N/20-KMnO ₄).	C. E.	Active O ₂ per K. W. H.
0.3 amp.	18.2	4.0 volts	6.0	53.6 %	40.00 g.
0.5	30.3	4.6	11.3	60.6	39.30
1.0	60.6	6.3	25.0	67.0	31.76
2.0	121.2	9.0	44.8	60.0	19.80
3.0	181.8	10.0	63.7	56.9	16.98

TABLE VI

Influence of cathodic current density on C. E.

Anodic C. D. = 60.6 amp./dm². Current used = 1 amp.

Other conditions, same as in Table V.

Cathodic C. D. (amp./dm ²).	P. D.	Active O ₂ in 5 c.c. of electrolyte soln. (in c.c. of N/20-KMnO ₄).	C. E.	Active O ₂ per K. W. H.
16.0	5.8 volts	25.0	67.0 %	34.48 g.
29.3	6.3	25.0	67.0	31.76
83.0	7.3	24.4	65.5	26.74

TABLE VII

Influence of inter-electrode distance on C. E.

Cathodic C. D. = 29.3 amps./dm². Other conditions same as in Table V.

Inter-electrode distance.	P. D.	Active O ₂ in 5 c.c. of electrolyte soln. (in c.c. of N/20-KMnO ₄).	C. E.	Active O ₂ per K. W. H.
1.1 cm.	5.3 volts	24.3	65.2 %	36.68 g.
3.1	6.3	25.0	67.0	31.76
4.0	7.3	26.7	71.3	29.26

TABLE VIII

Influence of diaphragm on C. E.

Anode placed in 50 c.c. of soln. placed in earthenware diaphragm, cathode in 60% H_2SO_4 soln. placed in outer glass cylinder. Inter-electrode distance=3.1 cm. Other conditions, same as in Table VII.

Expt No.	P. D.	Active O_2 in 5 c.c. of electrolyte soln. (in c.c. of $\text{N}/20\text{-KMnO}_4$).	C. E.	Active O_2 per K. W. H.
1	9.1 volts	30.6	82.1 %	26.90 g.
2*	9.4	33.5	90.0	28.42

*In this experiment KF (1 g./100 c.c. soln.) is used as addition agent along with the diaphragm.

TABLE IX

Influence of duration of electrolysis on C. E.

Inter-electrode distance=3.1 cm. Other conditions, same as in Table VII.

Duration.	P. D.	Active O_2 in 5 c.c. of electrolyte soln (in c.c. of $\text{N}/20\text{-KMnO}_4$).	C. E.	Active O_2 per K. W. H.
15 min.	6.3 ^a volts	13.0	69.8 %	36.19 g.
30	6.3	25.0	67.0	31.76
60	6.3	45.7	61.3	29.02
90	6.3	63.8	57.0	25.77
120	6.3	80.7	54.1	25.62
240	6.3	130.0	43.5	20.63

c

TABLE X

Influence of temperature on C. E.

Duration of electrolysis=30 minutes. Other conditions, same as in Table IX.

Temp.	P. D.	Active O_2 in c.c. of electrolyte soln (in c.c. of $\text{N}/20\text{-KMnO}_4$).	C. E.	Active O_2 per K. W. H.
5°	6.8 volts	25.4	68.1 %	29.88 g.
10°	6.3	25.0	67.0	31.76
15°	5.9	25.0	67.0	33.90
20°	5.6	22.5	60.3	32.14
30°	5.0	17.5	46.9	28.00
40°	4.8	12.3	33.0	20.50
50°	4.5	6.5	17.5	11.56
60°	4.3	2.8	7.5	5.41

TABLE XI

Influence of addition reagents on C. E.

Temperature of electrolysis = 10°. Addition agent in 100 c.c. of soln. = 1 g.
Other conditions, same as in Table X.

Addition agent added.	P. D.	Active O ₂ in 5 c.c. of electrolyte soln. (in c.c. of N/20-KMnO ₄).	C. E.	Active O ₂ per K. W. H.
NHl	6.3 volts	25.0	67.0 %	31.76 g.
KF	6.4	27.8	74.6	34.75
Na ₂ HPO ₄	6.2	26.8	71.9	34.59
HCl (conc.)	6.0	26.6	71.4	35.47
TiO ₂	6.3	26.3	70.5	33.40
V ₂ O ₅	6.3	26.1	70.0	33.14
CeO ₂	6.3	25.7	68.9	32.63
Na ₂ SO ₄	6.1	24.7	66.3	32.40
WO ₃	6.3	24.4	65.5	30.98
CaCl ₂	6.3	23.6	63.3	29.84
Pb(CH ₃ COO) ₂	6.1	23.5	63.0	30.82
ThO ₂	6.3	22.7	60.8	28.82
Fe ₂ (SO ₄) ₃	6.2	22.6	60.6	29.16
CoSO ₄ · 7H ₂ O	6.8	23.2	59.5	26.12
NaBr	5.9	21.4	57.4	29.02
K ₂ Cr ₂ O ₇	5.7	18.6	49.8	26.11
MnSO ₄ · 7H ₂ O	6.2	17.9	48.1	23.23
Tl(CH ₃ COO)	6.1	16.4	44.0	21.51
AgNO ₃	6.0	0	0	0

TABLE XII

Influence of cathode material on C. E.

Duration of electrolysis = 30 mins. Platinum electrode used in all the above series of experiments substituted by cheap materials. Other conditions, same as in Table X.

Cathode material.	P. D.	Active O ₂ in 5 c.c. of electrolyte soln. (in c.c. of N/20-KMnO ₄).	C. E.	Active O ₂ per K. W. H.
Platinum	6.3 volts.	25.0	67.0 %	31.76 g.
Brass	6.0	24.1	64.6	32.33
Lead	8.5	25.3	67.8	23.81
Graphite	7.0	24.8	66.5	28.34
Cadmium	7.0	25.1	67.3	28.68

DISCUSSION

Our foregoing results shown in Tables I to XII clearly indicate that the production of persulphates electrochemically is dependent on a wide variety of factors such as the composition of the electrolyte, the current density and the temperature, etc. When a neutral solution of magnesium sulphate was electrolysed between platinum electrodes at the operating conditions of temperature (10°) and current density (60.6 amp./dm^2) there was copious evolution of oxygen and hydrogen at the respective electrodes, accompanied by a faint smell of ozone, but practically there was no formation of persulphate (C. E. 2.2%). The presence of sulphuric acid, however, exerted marked influence on the formation of persulphuric acid (*cf.* Tables II and III).

Various views regarding the formation of persulphuric acid and persulphates exist in the literature. Of these the more important ones may be discussed. The dissociation of sulphuric acid in water takes place in two stages :



Reaction (1) is favoured by high concentration of the acid, whereas, reaction (2) is favoured in dilute solutions. By the polymerisation of HSO_4^- ions (Richarz, *Wied. Ann.*, 1885, **24**, 183; *Ber.*, 1888, **21**, 166), perdisulphuric acid, ($\text{H}_2\text{S}_2\text{O}_8$, Marshall's acid) is formed according to the equation,

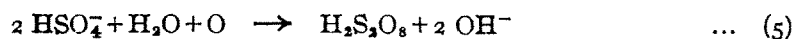


It follows therefore that a high concentration of HSO_4^- (ions) is the chief prerequisite if high yields of persulphate are required.

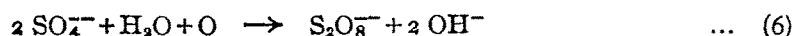
The unusually high yields of the persalt in the case of slightly acidic solutions of ammonium sulphate, where there is little probability of the presence of HSO_4^- ions, were tacitly assumed by Essin (*Z. Electrochem.*, 1933, **39**, 891) to be due to the polymerisation of SO_4^{--} ions according to the reaction,



An alternative general mechanism was suggested by Foerster ("Electrochemie Wasseriger Losungen", 1922, p. 842)

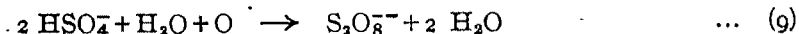
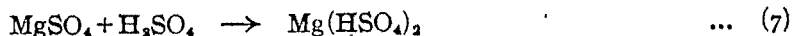


and in the particular case of the electrolysis of ammonium sulphate,



Very low (2.2%) or practically no production of persulphate obtained by the electrolysis of neutral solutions of magnesium sulphate might be attributed to the absence of HSO_4^- ions which are necessary [*cf.* reaction (3)]. With the progressive addition of sulphuric acid, however, the yield of persulphate increased steadily (*cf.* curve I, Fig 1). For example, the increase of concentration of H_2SO_4 from 20% to 60% with a concomitant increase of HSO_4^- ions increases the C. E. from 14.5% to 67%. Thus, it appears that

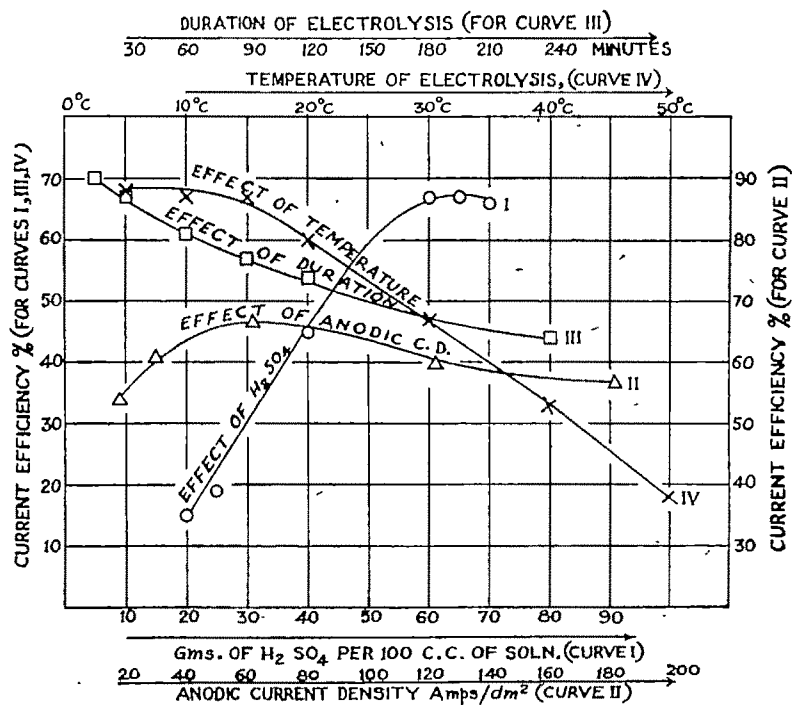
the formation of magnesium persulphate might, perhaps, be due to the following reactions. Magnesium sulphate in the presence of H_2SO_4 might form an acid sulphate,



thus accounting for the formation of magnesium persulphate. Even in slightly acidified solutions, progressive addition of MgSO_4 produces a corresponding increase in the C. E. (cf. Tables II, III and IV).

Variation of C. D. at the anode plays a very important rôle in all electrochemical oxidation reactions, especially in the formation of persulphates and persulphuric acid: A high anodic C. D. favours a high yield of persulphate. This is revealed by our results shown in Table V (curve No. II). This might probably be due to the discharge potential of HSO_4^- ions being higher than that of SO_4^{--} ions or of oxygen. Our results indicate that optimum yields of persulphate are obtained at C. D. of 68 amp./dm². It may also be probable that the close packing of HSO_4^- ions, which might result at such high anodic C. D., might contribute to an increase in the C. E. The variation of C. D. at the cathode (cf. Table VI) shows very little influence on the C. E. of persulphate formation.

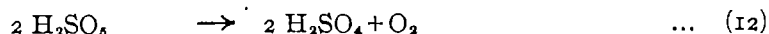
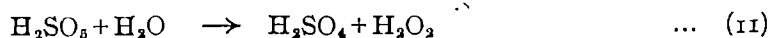
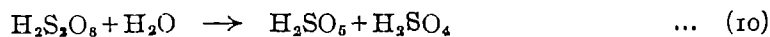
FIG. I



In oxidation reactions in a cell without a diaphragm, the oxidation products formed at the anode might diffuse to the cathode and get reduced by the nascent hydrogen

released at the cathode. An increase in the inter-electrode distance, it is to be anticipated, might minimise the possible reduction at the cathode and thereby increase the yield of persulphate, a deduction in close accord with our experimental results (cf. Table VIII). This is further supported by our results showing marked increase in the C. E. from 67% to 82.1% by carrying out the electrolysis in a diaphragm cell which prevented the oxidised products from being reduced by diffusion. But it should also be noted that with the use of diaphragm, the P. D. across the cell increases considerably from 6.3 to 9.1 volts. This brings about an increase in the consumption of electrical energy which is not technically desirable.

Our results in Table IX (cf. Fig 1, curve III) indicate that the C. E. falls gradually with progressive duration of electrolysis, but this fall is very much less steep than what is obtained in the case of electrolysis of H_2SO_4 (Solanki and Sheshadri, unpublished work). In the electrolysis of 60% H_2SO_4 a 'steady state' is reached after a comparatively short time, practically there being no further increase in the amount of persulphuric acid with the prolongation of electrolysis, the rate of formation of persulphuric acid being equal to the rate of destruction of the peracid, especially Caro's acid (*vide supra*). This is due to the conversion of $\text{H}_2\text{S}_2\text{O}_8$ into highly unstable (readily decomposing) Caro's acid, which might also function as a depolariser, thus reducing the C. E.



But in the electrolysis of a solution containing 45% $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ and 60% H_2SO_4 , our results indicate that the C. E. remains sufficiently high even after longer intervals and there is no attainment of the steady state. This might perhaps be due to the absence of Caro's acid and also due to the fact that the cation Mg^{++} might inhibit the decomposition of the persulphate ion, $\text{S}_2\text{O}_8^{--}$, and thereby stabilise the product.

The variation of temperature affects the yield of persulphate considerably. In general, low temperatures are favourable for high yields of persulphates (cf. Table X, Fig 1, curve IV). The C. E. is fairly constant between 5° and 15°. At higher temperatures the persalt MgS_2O_8 might undergo the decomposition due to the reaction with H_2SO_4 forming $\text{H}_2\text{S}_2\text{O}_8$, the latter undergoing stepwise hydrolytic decomposition and chemical decomposition [cf. equations (10), (11), (12)] and this might lower the yields of the persalts.

Addition agents like KF, HF, HCl show pronounced beneficial effect in improving the yield of the persulphate obtained electrolytically.

The function of these substances is probably due to

(1) an increase of anode potential, and (2) destruction of Caro's acid chemically thus preventing its depolarisation or chemical decomposition.

The amount of addition agent added in each of these experiments was 1 g. per 100 c.c. of the solution and the order of their influence was as : $\text{KF} > \text{Na}_2\text{HPO}_4 > \text{HCl} \geq \text{TiO}_2 \geq \text{V}_2\text{O}_5 \geq \text{CeO}_2$ etc. The highly beneficial effect of KF might be due to

the slight increase in the anodic potential. HCl and Na_2HPO_4 increased the C. E., though the P. D. decreased, probably due to chemical destruction of Caro's acid. $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7$ reduced the C. E. considerably, processes other than the formation of $\text{H}_2\text{S}_2\text{O}_8$ such as cyclic oxidation and reduction of Mn and Co ions might be taking place. With the addition of AgNO_3 , however, the yield dropped down to zero. This marked inhibitory action of AgNO_3 might, perhaps, be due to a lowering of the anodic potential from 6.3 to 6.0 volts or to its catalytic action on the decomposition of the persalts, no sooner they are formed. By the addition of KF to the electrolyte in a diaphragm cell, the C. E. might be raised to as high a value as 92% (cf. Table VIII).

An attempt was made to find out cheap substitutes in place of platinum as the cathode material. Several cathodes were tried and results showed (cf. Table XII) that the operation was smooth with platinum cathode and the P. D. (corresponding energy consumption) was minimum for the same yield of the persalt.

The authors express their indebtedness to Principal Dr. S. S. Joshi, D. Sc., for his valuable help and criticism during the course of this work.

ELECTROCHEMICAL LABORATORY,
BENARES HINDU UNIVERSITY.

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A METHOD FOR THE SYNTHESIS OF LACTONES OF SUBSTITUTED CROTONIC ACIDS. CONDENSATION OF β -ARYL GLUTACONIC ANHYDRIDES WITH PHENOLIC ETHERS

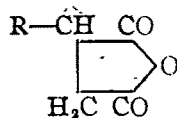
BY V. M. BHAVE AND R. V. BHAGWAT

A general method for the synthesis of various lactones of substituted crotonic acids has been worked out by the condensation of β -aryl substituted glutaconic anhydrides with phenolic ethers in the presence of anhydrous $AlCl_3$. The corresponding lactones in the case of *o*-(4-methoxyphenyl)-glutaconic anhydride and (i) anisole, (ii) *o*-cresol methyl ether and (iii) thymol methyl ether have been obtained in good yield. This type of lactones might be expected to have good anthelmintic properties.

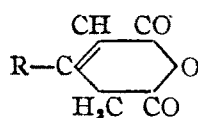
Santonin possesses vermifugal properties, which have been attributed to the presence of a "lactonic ring" in the substance. The property was also shown to be possessed by various other substituted lactones (Trendelenburg, *Arch. Exp. Path. & Pharm.*, 1916, 79; Oettingen, *J. Pharm. Exp. Therp.*, 1929, 36, 335; *J. Amer. Chem. Soc.*, 1930, 52, 2025; Rosenmund and Shapiro, *Arch. Pharm.*, 1934, 272, 313).

Nargund and co-workers (*J. Univ. Bom.*, 1940, 9, III, 145; 1941, 10, III, 99; 1942, 11, 124; 1943, 11A, 104; *Rasayanam*, 1943, 1, 233; *Proc. Ind. Acad. Sci.*, 1944, 19A, 381; *J. Univ. Bom.*, 1944, 13, 22) prepared substituted butyrolactones some of which they claim to have superior anthelmintic properties. They have obtained these lactones starting with the condensation of aryl-substituted succinic anhydrides with phenolic ethers.

The β -aryl glutaconic anhydrides (Limaye and Bhavé, *J. Indian Chem. Soc.*, 1931, 8, 137; Limaye and Gogte, *J. Univ. Bom.*, 1934, 3, III, 135; Dixit and Gokhale, *ibid.*, 1934, 3, III, 80; Bhavé, Ph. D. Thesis, Univ. Bom., 1942) differ from the aryl substituted succinic anhydrides only by one CH_2 group and a double bond.

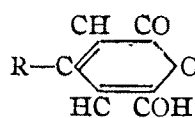


Aryl substituted succinic anhydride.



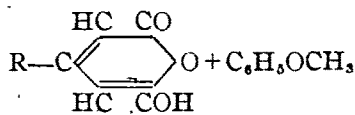
(Normal form)

β -Aryl glutaconic anhydride.

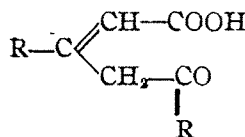


(Enolic form)

These β -aryl glutaconic anhydrides were therefore expected to give the corresponding crotonic acids and the lactones as observed by Bhavé (*Rasayanam*, 1941, Nov. 6).

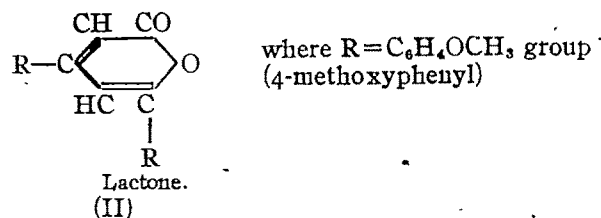


β -Aryl glutaconic anhydride.



(I)

β -Substituted crotonic acid.



Gogte, however, had reported that such a reaction did not take place in the case of *p*-cresol ethyl ether and β -(2-ethoxy-5-methylphenyl)-glutaconic anhydride (*Proc. Ind. Acad. Sci.*, 1935, 2A, 185). He attributed the failure to the presence of unsaturation in the side-chain of the glutaconic anhydride.

In view of these conflicting observations it was thought necessary to confirm the structures of the above products of condensation (Bhave, *loc. cit.*).

The Lactone of β -(4-Methoxyphenyl)- γ -(4-methoxybenzoyl)-crotonic Acid

This lactone (A, m. p. 174°) was prepared by condensing the β -(4-methoxyphenyl)-glutaconic anhydride with anisole in the presence of anhydrous AlCl_3 . It was also accompanied with a small quantity of the corresponding acid (B), m. p. 132° .

The structure of the lactone and the acid were confirmed as follows:

(1) The lactone (A, m. p. 174° ; $\text{C}_{19}\text{H}_{18}\text{O}_4$) could be converted into the acid (B, m. p. 132° ; $\text{C}_{19}\text{H}_{18}\text{O}_5$) by the action of alcoholic alkali and the acid (B) into the lactone (A) by the action of acetic anhydride or mineral acids.

(2) On decarboxylation the acid (B) gave a ketone (C), m. p. 97° , $\text{C}_{18}\text{H}_{18}\text{O}_3$.

(3) On oxidation the acid (B) as also the ketone (C) gave only *anisic acid*.

(4) The acid (B) gave a high melting (above 300°), brightly coloured pyrylium derivative showing the presence of a COCH_3 -group (Decker and Fellenburg, *Annalen*, 1907, 356, 302; Perkin, Robinson and Turner, *J. Chem. Soc.*, 1908, 93, 1085; Dalal, Bokil and Nargund, *J. Univ. Bom.*, 1939, 8, III, 190).

(5) On reduction the acid (B) took up two hydrogen atoms to give a ketonic acid (D, m. p. 125° ; $\text{C}_{19}\text{H}_{20}\text{O}_5$) from which the usual ketonic derivatives were prepared.

(6) The structure of the acid (D, m. p. 125°) was further confirmed by preparing it by condensing the β -(4-methoxyphenyl)-glutaric anhydride with anisole.

On the basis of the foregoing evidence the structures of the acid (B) and the lactone (A) must be represented by (I) and (II) above respectively *i.e.*, (A) is the lactone of the acid (B) which is β -(4-methoxyphenyl)- γ -(4-methoxybenzoyl)-crotonic acid, which thus confirms the structures, provisionally assigned to them by Bhave (*loc. cit.*).

The above reaction between β -aryl glutaconic anhydrides and phenolic ethers has been found to be of general and wide application and the extension of the reaction to the condensation of β -(4-methoxyphenyl)-glutaconic anhydride with *o*-cresol methyl ether and thymol methyl ether has also been carried out with similar results.

EXPERIMENTAL

(1) *Lactone of β -(4-Methoxyphenyl)- γ -(4-methoxybenzoyl)-crotonic Acid.*— β -(4-Methoxyphenyl)-glutaconic anhydride (2.18 g.) and anisole (1.08 g.) were dissolved in distilled

nitrobenzene (10 c. c.) and freshly powdered anhydrous AlCl_3 (3 g.) was slowly added. After 4 hours it was poured into about 80 c. c. of cold water and 10 c. c. of conc. HCl . The nitrobenzene was removed by steam distillation. The reaction product was washed first with water and then rubbed in a mortar with dilute solutions of Na_2CO_3 and NaOH and again with water. [These alkaline washings on acidification with dil. HCl gave a small amount (0.150 g.) of the acid of m. p. 132° , described below.] The solid remaining behind was dried and crystallised from alcohol in lemon-yellow crystals, m. p. 174° , yield 2.0 g. It is neutral in reaction and does not give any coloration with FeCl_3 . (Found: C, 74.06; H, 5.41. $\text{C}_{10}\text{H}_{10}\text{O}_4$ requires C, 74.02; H, 5.19 per cent). By the action of alcoholic alkalis it gave the acid, m. p. 132° , as described below.

(2) β -(4-Methoxyphenyl)- γ -(4-methoxybenzoyl)-crotonic Acid.—As mentioned above, this acid was obtained on acidification of the alkaline washings of the lactone of m. p. 174° . It could be also obtained from the lactone by the action of alcoholic alkalis.

The above lactone (2 g.) was dissolved in boiling ethyl alcohol and a solution of NaOH (4 g.) in 10 c. c. of water was added. It was heated on a water-bath for 15 minutes, a further quantity of water added, and the alcohol evaporated off. The alkaline filtrate was acidified with HCl (1 N) and the acid obtained could be purified by crystallisation from ethyl alcohol, 50% acetic acid or from water in white, silky needles, m.p. 132° (decomp.). [Found: C, 69.81; H, 5.47; equiv., 327.5. $\text{C}_{10}\text{H}_{10}\text{O}_5$ requires C, 69.93; H, 5.22 per cent. Equiv. (monobasic), 326].

The acid is very sensitive towards the action of mineral acids such as HCl , H_2SO_4 as also acetic anhydride and is converted into the lactone, m.p. 174° .

The acid gives the methyl ester, m.p. 51° (by the silver salt method) and the dark orange pyrylium derivative (m.p. above 300°) is obtained when the acid is treated with salicyl aldehyde in the presence of dry HCl gas.

(3) β -(4-Methoxyphenyl)-propylene-(4-Methoxyphenyl) Ketone.—The above acid (1 g.) was heated slightly above its melting point in an oil-bath, when it decomposed and gave off CO_2 . It was cooled and the solid mass was washed with a small amount of NaHCO_3 solution and then with water. It was crystallised from alcohol, m.p. 97° . (Found: C, 76.44; H, 6.3. $\text{C}_{18}\text{H}_{18}\text{O}_3$ requires C, 76.61; H, 6.38 per cent).

When oxidised with KMnO_4 by dissolving the ketone in acetone solution, anisic acid was obtained. This ketone gave phenylhydrazone ($\text{C}_{24}\text{H}_{24}\text{O}_2\text{N}_2$), m.p. 126° .

(4) β -(4-Methoxyphenyl)- γ -(4-Methoxybenzoyl)butyric Acid.—The acid of m.p. 132° (1 g.) was dissolved in just sufficient quantity of 0.5N- NaOH solution to which 4% sodium amalgam (10 g.) was slowly added in small portions at a time. The reaction mixture was vigorously shaken for about 45 minutes. After the cessation of evolution of hydrogen, the solution was filtered and the filtrate acidified with dilute HCl . The sticky mass was washed with water. After solidification it was powdered and treated with about 2% NaHCO_3 solution (30 c.c.). The filtrate was acidified with dilute HCl and the white precipitate obtained was crystallised from dilute acetic acid, m.p. 125° . [Found: C, 69.36; H, 5.97; equiv., 329.4. $\text{C}_{10}\text{H}_{10}\text{O}_5$ requires C, 69.5; H, 6.096 per cent. Equiv. (monobasic), 328].

This acid is ketonic in nature and affords a semicarbazone ($\text{C}_{20}\text{H}_{20}\text{O}_5\text{N}_2$), m.p. 219° ; a phenylhydrazone ($\text{C}_{20}\text{H}_{18}\text{O}_5\text{N}_2$), m.p. 176° and an oxime ($\text{C}_{10}\text{H}_{11}\text{O}_5\text{N}$), m.p. 174° .

The acid (m.p. 125°) was found identical with an acid obtained by the condensation of β -(4-methoxyphenyl)-glutaric anhydride with anisole in the presence of anhydrous AlCl_3 . The identity was confirmed by the mixed melting points of the acid as well as of its derivatives.

(5) *Lactone of the β -(methoxyphenyl)- γ -(3-methyl-4-methoxybenzoyl)-crotonic acid* was prepared by the same method as described under (1), by using 2.18 g. of the β -(4-methoxyphenyl)-glutaconic anhydride, 1.22 g. of *o*-cresol methyl ether, 10 c.c. of nitrobenzene and 3.0 g. of powdered anhydrous AlCl_3 . The lemon-yellow lactone melts at 176° . (Found: C, 74.25; H, 5.68. $\text{C}_{20}\text{H}_{18}\text{O}_4$ requires C, 74.52; H, 5.59 per cent).

When treated with alcoholic alkali (as in expt, No. 2) it gave the β -(4-methoxyphenyl)- γ -(3-methyl-4-methoxyphenyl)-crotonic acid, m.p. 131° . [Found: C, 70.41; H, 5.78; equiv. 340.8. $\text{C}_{20}\text{H}_{20}\text{O}_5$ requires C, 70.58; H, 5.882 per cent. Equiv. (monobasic), 340].

This acid (m.p. 131°) when treated with salicyl aldehyde in the presence of dry HCl gas gave a pyrylium derivative.

When the acid was decarboxylated by heating it above its melting point, it lost CO_2 and gave rise to the ketone, m.p. 84° , $\text{C}_{19}\text{H}_{20}\text{O}_3$ i.e., the β -(4-methoxyphenyl)-propylene-(3-methyl-4-methoxyphenyl)-ketone. It gave a phenylhydrazone, m.p. 134° .

(6) *The lactone of the β -(4-methoxyphenyl)- γ -(2-methyl-4-methoxy-5-isopropylbenzoyl)-crotonic acid* was prepared by using 2.18 g. of the β -(4-methoxyphenyl)-glutaconic anhydride, 1.64 g. of thymol methyl ether, 10 c.c. of nitrobenzene and 3 g. of powdered anhydrous AlCl_3 , by the same method as that described in expt. No. 1. Unlike the lactones described above this lactone is quite colourless in appearance and easily soluble in alcohol, m.p. 126° . (Found: C, 75.73; H, 6.725. $\text{C}_{23}\text{H}_{24}\text{O}_4$ requires C, 75.82; H, 6.594 per cent).

β -(4-Methoxyphenyl)- γ -(2-methyl-4-methoxy-5-isopropylbenzoyl)-crotonic Acid.—When treated with 30% solution of NaOH (by dissolving the lactone in alcohol) an acid (m.p. 74°) with an equivalent of 378.2 was obtained. (A monobasic acid with the formula $\text{C}_{23}\text{H}_{24}\text{O}_5$ requires the equivalent 382).

The authors take this opportunity to express their thanks to the authorities of Ramnarain Ruia College for granting them facilities to carry out the above work.

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RAMNARAIN RUIA COLLEGE,
MATUNGA, BOMBAY. 19.

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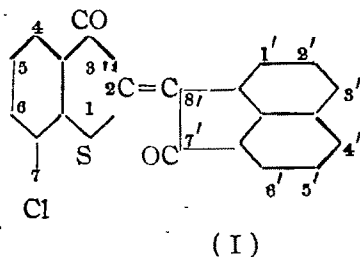
DYES DERIVED FROM ACENAPHTHENEQUINONE. PART X. 2-(7-CHLORO)-THIONAPHTHENE-ACENAPHTHYLENE INDIGOS

BY SISIR KUMAR GUHA AND JNANENDRA NATH CHATTERJEE

7-Chloro-3-hydroxythionaphthene has been condensed with acenaphthenequinone and some of its important derivatives and also aceanthrenequinone. The thioindigoid dyes of the 7-chloro series, described here, are lighter than those of the 5-chloro compounds studied previously.

This communication is an extension of the work of Guha (*J. Indian Chem. Soc.*, 1933, 10, 679; 1936, 13, 94; 1938, 15, 20; 1943, 20, 37; 1944, 21, 91) which was studied with the object of examining the effect of a methyl radical when present in every available position of the thionaphthene ring of 2-thionaphthene-acenaphthylene indigos (Ciba scarlet G, Ciba red R etc.).

It deals with the preparation and a study of the properties of 2-(7-chloro)-thionaphthene-acenaphthylene indigos which represent a new series of thioindigoid vat dyes of asymmetrical character and possess the general structural formula (I).



Acenaphthenequinone, its 3-chloro, 3-bromo and 1-methoxy derivatives have been condensed with 7-chloro-3-hydroxythionaphthene (Dalglish and Mann, *J. Chem. Soc.*, 1945, 893) respectively and the corresponding thioindigoid vat dyes obtained. These are yellowish red, red and deep red crystalline compounds, soluble in pyridine, xylene and nitrobenzene. The parent dye and its 3'-chloro and 3'-bromo derivatives are soluble in benzene, while the 1'-methoxy derivative is moderately soluble in the same solvent. They are all sparingly soluble in alcohol and CCl_4 except the 3'-chloro compound, which is moderately soluble in the latter.

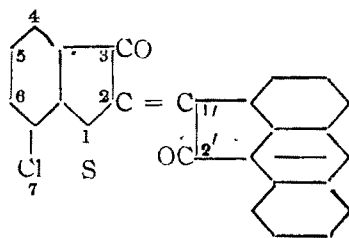
In this class of dyes, the vat is produced between 50° and 60° by the action of alkaline hydrosulphite; it is noticed that during reduction, excess of caustic alkali turns the vat into a tarry product and hence it is carefully avoided. The dyeing shades were uniformly and fully developed on cotton from the hydrosulphite vat except in the case of the methoxy compound. Even after prolonged treatment the vat obtained from the 1'-methoxy dye was faint violet from which an uniform pink colour developed on atmospheric oxidation (*cf.* Goldstein and Schlenker, *Helv. Chim. Acta*, 1921, 4, 234; Guha, *loc. cit.*, *J. Indian Chem. Soc.*, 1939, 16, 127).

The dyeing shades, obtained from the compounds of this series, on wool from a dilute sulphuric acid bath are also quite uniform. Although lighter, these are more pleasant than those obtained from the 3-indole-2'-(7'-chloro)-thionaphthene indigos (Guha and Chatterjee, this *Journal*, 1947, 28, 473). A study of the colour of the compounds described here and their dyeing shades indicate (Table I) that they are lighter than those of the corresponding substances belonging to the 2-(5-chloro)-thionaphthene-acenaphthylene indigo series (Guha, *loc. cit.*). A quantitative measurement of the change in colour due to the effect of a chlorine atom in the 5'-position and in the 7'-position of the thionaphthene ring of 2-thionaphthene-acenaphthylene indigos will be communicated afterwards.

TABLE I

A = acenaphthylene indigo	T = Thionaphthene.
Compounds.	Dyeing shade on cotton.
{ 2-(5-Chloro) T-A { 2-(7-Chloro) T-A	Dark red Red
{ 2-(5-Chloro) T-8'-(3'-chloro)-A { 2-(7-Chloro) T-8'-(3'-chloro)-A	Dark red Red
{ 2-(5-Chloro) T-8'-(3'-bromo)-A { 2-(7-Chloro) T-8'-(3'-bromo)-A	Dark red Deep red
{ 2-(5-Chloro) T-8'-(1'-methoxy)-A { 2-(7-Chloro) T-8'-(1'-methoxy)-A	Pink Pink (lighter shade)

Another asymmetrical thioindigoid dye, 2-(7-chloro)-thionaphthene-1'-aceanthrylene indigo (II), has also been obtained now by condensing aceanthrenequinone (Liebermann and Zsuffa, *Ber.*, 1911, 44, 209) with 7-chloro-3-hydroxythionaphthene. It is a brown colouring substance and lighter than that of the 2-(7-chloro)-thionaphthene-acenaphthylene indigo (*loc. cit.*) which is yellowish red.



(II)

EXPERIMENTAL

2-(7-Chloro)-thionaphthene-acenaphthylene indigo.—Acenaphthene quinone (0.546 g.) and 7-chloro-3-hydroxythionaphthene (0.5535 g.) were dissolved in boiling glacial acetic acid (55 c. c.) and treated with strong hydrochloric acid (3.5 c. c.); the mixture was shaken when the crystalline yellowish red dye separated as a thick mass. Glacial acetic acid (70 c. c.) was further added and boiled for 25 a minutes, filtered hot, washed with

a little acetic acid and hot water, yield 0.745 g. It was crystallised from nitrobenzene in long, silky, pointed needles, m. p. $313-14^{\circ}$. It is soluble in acetic acid; strong sulphuric acid dissolves it producing a green solution. It dyes wool in yellowish red shade from an acid bath, and cotton in pleasant and attractive red shade from the violet vat formed by the action of alkaline hydrosulphite. (Found: C, 68.6; H, 2.6. $C_{20}H_8O_2ClS$ requires C, 68.89; H, 2.58 per cent).

2-(7-Chloro)-thionaphthene-8'-(3'-chloro)-acenaphthylene indigo was similarly prepared from 3-chloroacenaphthenequinone (0.6495 g.) and 7-chloro-3-hydroxythionaphthene (0.5535 g.) in hot glacial acetic acid (70 c. c.) and strong hydrochloric acid (4 c. c.). The mixture containing the lumpy mass of the separated dye was again treated with glacial acetic acid (20 c. c.) and boiled for 25 minutes. The wooly, long, needle shaped red dye (0.879 g.) was crystallised from xylene in thin needles, m. p. $292-93^{\circ}$. It is moderately soluble in acetone. The solution of the substance in strong sulphuric acid is light green. The dyeing shade on wool is similar to, but slightly deeper than that obtained from the preceding compound. It dyes cotton in red shade from the blue alkaline hydrosulphite vat. (Found: C, 62.1; H, 2.3. $C_{20}H_8O_2Cl_2S$ requires C, 62.66; H, 2.08 per cent).

2-(7-Chloro)-thionaphthene-8'-(3'-bromo)-acenaphthylene indigo separated in deep red crystalline mass (0.678 g.) when a solution of 3-bromoacenaphthenequinone (0.652 g.) and 7-chloro-3-hydroxythionaphthene (0.4612 g.) in glacial acetic acid (100 c. c.) was treated with strong hydrochloric acid (5 c. c.) and boiled for 20 minutes. It was crystallised from xylene in wooly clusters of needles, m. p. $281-83^{\circ}$. It is moderately soluble in acetic acid; it dissolves in strong sulphuric acid producing a light blue solution. It dyes wool from an acid bath in yellowish red shade which is deeper than those obtained from the 3'-chloro and the mother compound. Cotton is dyed in pleasant deep red shade from the violet-blue alkaline hydrosulphite vat. (Found: C, 55.4, 55.6; H, 1.8, 1.9. $C_{20}H_8O_2ClBrS$ requires C, 56.14, H, 1.87 per cent).

2-(7-Chloro)-thionaphthene-8'-(1'-methoxy)-acenaphthylene indigo.—The light red solution, produced by dissolving β -methoxyacenaphthenequinone (0.742 g.) and 7-chloro-3-hydroxythionaphthene (0.6457 g.) in glacial acetic acid (125 c. c.), on treatment with strong hydrochloric acid (5 c. c.) and boiling for 25 minutes separated a darkish red, fibrous crystalline dye (0.5812 g.). It was crystallised from nitrobenzene in wooly needles not melting below 320° . It is moderately soluble in benzene and acetic acid. The colour of the solution of the dye in strong sulphuric acid resembles that of the preceding compound. It dyes wool in darkish red from an acid bath and cotton in pink colour from the faint violet hydrosulphite vat. (Found: C, 66.1; H, 3.3. $C_{21}H_{11}O_2ClS$ requires C, 66.58; H, 2.9 per cent).

2-(7-Chloro)-thionaphthene-1'-aceanthrylene-indigo.—Aceanthrenequinone (0.696 g.) and 7-chloro-3-hydroxythionaphthene (0.5535 g.) were dissolved in boiling glacial acetic acid (125 c. c.) and treated with strong hydrochloric acid (6 c. c.). It was boiled for 30 minutes during which the brown crystalline dye separated gradually. The dye (0.682 g.) was washed successively with glacial acetic acid and dilute sodium hydroxide and finally with hot water. It was crystallised from nitrobenzene in small clusters of fibrous

needles not melting below 320° . It is soluble in pyridine, xylene, nitrobenzene and benzene; moderately soluble in glacial acetic acid; sparingly soluble in carbon tetrachloride; insoluble in alcohol. The solution of the substance in strong sulphuric acid is light green. It dyes wool in brown shade from an acid bath and cotton in red ochre shade from the light yellow hydrosulphite vat. (Found: C, 72.1; H, 2.3. $C_{24}H_{11}O_2ClS$ requires C, 72.28; H, 2.75 per cent).

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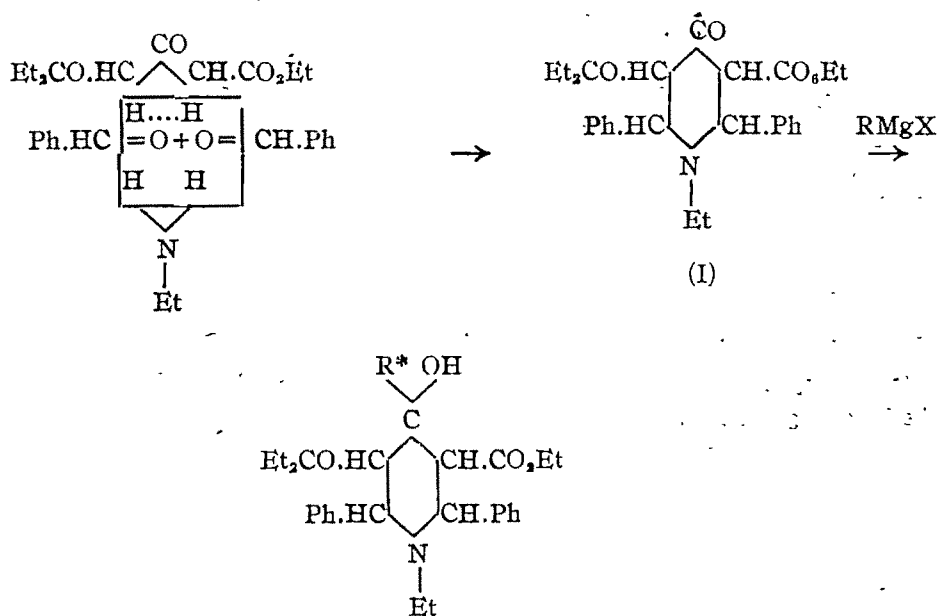
Received May 3, 1948.

SYNTHESIS OF PIPERIDINE DERIVATIVES. PART II

By A. B. SEN AND G. S. SIDHU

Diethyl 1-ethyl-2:6-diphenyl-4-oxo-4-ethyl (and 4-phenyl)-piperidine-3:5-dicarboxylates have been synthesised by the action of the appropriate Grignard reagent on diethyl 1-ethyl-2:6-diphenyl-4-piperidone-3:5-dicarboxylate. The high and the low melting varieties of the latter, mentioned by Petrenko-Kritschenko have now been shown to be keto and enol forms.

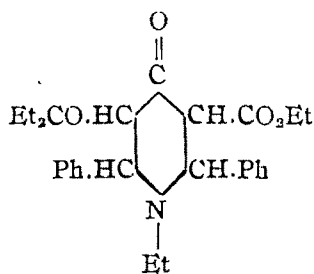
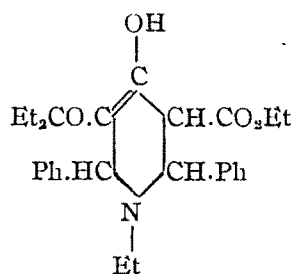
In a previous paper (this *Journal*, 1947, **24**, 293) the preparation of four substituted N-methyl- γ -piperidols by the action of different alkyl or aryl magnesium halides on substituted N-methyl- γ -piperidones has been described. Considerable work in these lines has been done in recent years with unsubstituted N-alkyl-piperidones and the piperidols, thus obtained, and their esters have been examined for analgesic properties (John Lee *et al.*, *J. Organic Chem.*, 1947, **12**, 885; Ziering *et al.*, *ibid.*, 894; Berger *et al.*, *ibid.*, 904; Ziering and Lee, *ibid.*, 911). In this paper the work has been extended for the preparation of substituted N-ethyl- γ -piperidols by the action of the appropriate Grignard reagent on diethyl 1-ethyl-2:6-diphenyl-4-piperidone-3:5-dicarboxylate (I).



II (R=Et) and III (R=Ph)

The action of *n*-butyl- and *n*-propylmagnesium bromides on the above piperidone was also tried but the end-product in both cases was a pasty mass which could neither be crystallised nor distilled in high vacuum.

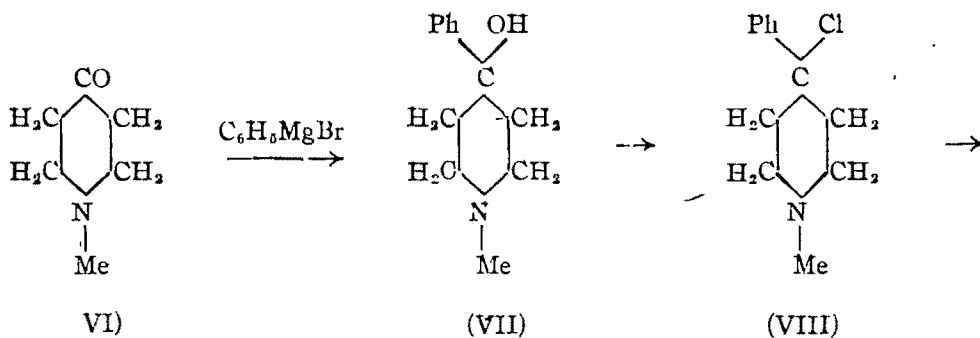
The piperidone (I), used in these reactions, was first prepared by Petrenko-Kritschenko (*Ber.*, 1909, **42**, 3689) who obtained it in two distinct forms with different melting points (92° and $137-40^{\circ}$). He did not, however, offer any explanation of this phenomenon and just referred to these modifications as the higher and lower melting forms. The lower melting point form was obtained by the action of gaseous ethylamine on a cooled mixture of benzaldehyde and ethyl acetone-dicarboxylate. The higher melting point form resulted if liquid ethylamine was used. The present authors at first used ethylamine in alcoholic solution and the result was a mixture of both the forms which could be separated by careful fractional crystallisation from ethyl alcohol, the solubility of the lower melting form being greater. The present authors have further shown these to be keto-enol isomers, both forms being capable of separate stable existence.

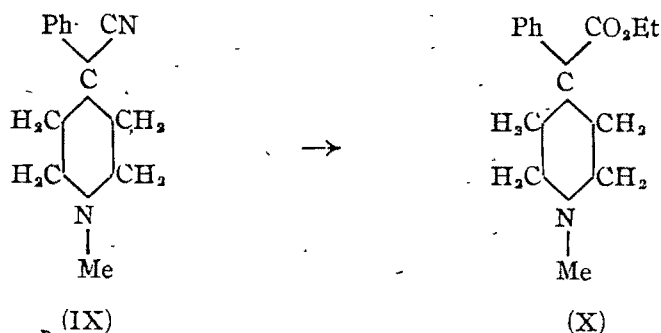
(IV, m. p. $137-40^{\circ}$)(V, m. p. 92°)

The compound with the higher melting point has been shown to be the keto form (IV) by preparing its 2:4-dinitrophenylhydrazone. It does not decolorise bromine water and after two recrystallisations gives no coloration with ferric chloride in cold alcoholic solution.

The compound with the lower melting point, on the other hand, immediately gives a red coloration with ferric chloride and also rapidly decolorises bromine water, and is thus in all probability of the enol form (V).

A new synthesis of the well known analgesic, Dolantin, was undertaken according to the following scheme :—





But it was found that N-methyl- γ -piperidone (VI) was difficult to prepare, as starting from 85 g. of ethyl β -bromopropionate (prepared from ethylene chlorohydrin) only 7 g. of the piperidone (VI) could be obtained by the method of McElvain (*J. Amer. Chem. Soc.*, 1924, **46**, 1721; 1929, **51**, 922). This on reacting with phenylmagnesium bromide gave the desired piperidol (VII), but in a yield not sufficient for further reaction and characterisation. The proposed synthesis had perforce to be shelved pending the arrival of ethyl acrylate which would simplify the preparation of the piperidone (VI). Attempts to prepare this piperidone by the Mannich reaction from methylamine, formaldehyde and ethyl acetone-dicarboxylate did not succeed.

EXPERIMENTAL

Diethyl 1-Ethyl-2:6-diphenyl-4-piperidone-3:5-dicarboxylate (I).—A mixture of ethyl acetone-dicarboxylate (14 g.) and freshly distilled benzaldehyde (7 g.) was strongly cooled in ice and salt and chilled anhydrous ethylamine (3.4 g.) added to it. The mixture was shaken for 15 minutes and then left overnight in the refrigerator. The next day the solid mass was filtered off with the addition of 30 c.c. of ice-cold ether and recrystallised from hot alcohol, m. p. 135–37°, yield 12 g.

When in the above preparation anhydrous ethylamine was substituted by a 30% alcoholic solution of ethylamine, the result was a mixture of the above keto form (I or IV) and the enol form (V). The pasty mass obtained was dissolved in the minimum quantity of boiling ethyl alcohol and filtered hot. The keto form separated on cooling and was collected at the pump and the enol form obtained by the slow evaporation of alcohol from the mother-liquor, m. p. 92°.

2:4-Dinitrophenylhydrazone of (I) was prepared in the usual manner from (I) and 2:4-dinitrophenylhydrazine in absolute alcohol and concentrated sulphuric acid, m. p. 171°. (Found: N, 12.11. $C_{31}H_{25}O_5N_5$ requires 11.80 per cent).

Diethyl 1-ethyl-2:6-diphenyl-4-oxy-4-phenylpiperidine-3:5-dicarboxylate (III) was prepared by the action of phenylmagnesium bromide [obtained from 0.24 g. (0.01 mole) magnesium and 1.6 g. (0.01 mole) bromobenzene in 50 c.c. dry ether in an atmosphere of nitrogen] on 4.2 g. (0.01 mole) of the piperidone (I) dissolved in dry ether. The experimental details were the same as described in the previous paper (Zaheer, Sen and Sidhu, *J. Indian Chem. Soc.*, 1947, **24**, 293). The Grignard complex was

decomposed by ice-cold dilute sulphuric acid and the piperidol (III) liberated was washed with a little cold ether to remove some diphenyl formed during the reaction. It was recrystallised from boiling alcohol in white leaflets, m. p. 151-52°, yield 2.5 g. (Found: N, 3.20. $C_{31}H_{33}O_5N$ requires N, 2.70 per cent).

Diethyl 1-ethyl-2:6-diphenyl-4-oxy-4-ethylpiperidine-3:5-dicarboxylate (II) was prepared as above by the action of ethylmagnesium iodide (obtained from 0.18 g. of magnesium and 1.2 g. ethyl iodide in 30 c.c. dry ether) on 3.0 g. of the piperidone (I). It crystallised as white leaflets from boiling alcohol, m. p. 142-43°, yield 2.0 g. (Found: 3.54. $C_{27}H_{33}O_5N$ requires N, 3.10 per cent).

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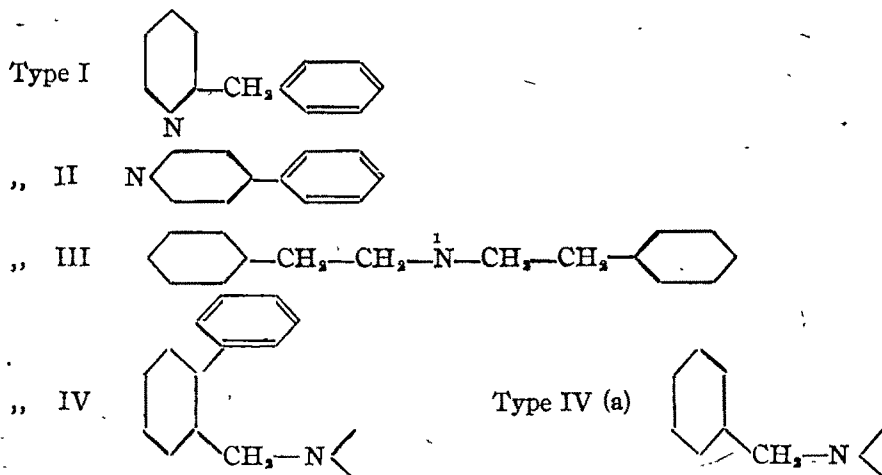
Received April 15, 1948

SYNTHESIS OF 4-QUINAZOLOLS. PART I

By A. B. SEN AND G. S. SIDHU

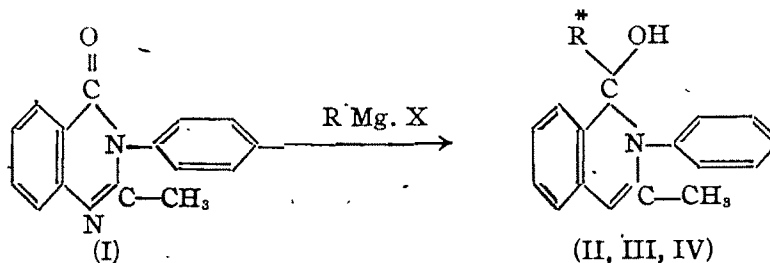
Three substituted 4-quinazolols have been prepared with a view to testing them for analgesic properties.

The search for synthetic analgesics, based on the partial structures of morphine, has led to several investigations in recent years (Kirkpatrick and Parkar, *J. Amer. Chem. Soc.*, 1935, **57**, 1123; Cassaday and Bogert, *ibid.*, 1939, **61**, 3055; Schaumann, *Arch. exp. Path. Pharm.*, 1940, **196**, 104; Harnest and Burger, *J. Amer. Chem. Soc.*, 1943, **65**, 370; Cook and Read, *J. Chem. Soc.*, 1945, 399; Anker, Cook and Heilbron, *ibid.*, 1945, 917; Anker and Cook, *ibid.*, 1946, 58). The most comprehensive work in this direction has been carried out by Lee *et al.*, Borell Jubilee Volume, Basle, 1946, pp. 264-305), and the synthesis of the compounds containing partial morphine structures has been exhaustively studied. They have divided these compounds into the following four types :



Compounds of type II were obtained by the action of Grignard reagents on N-alkyl γ -piperidones. It may be recalled that the present authors have been independently carrying out similar syntheses with substituted N-alkyl γ -piperidones, obtained by the Mannich reaction (this *Journal*, 1947, **24**, 293; 1948, **25**, 433).

With a view to studying the effect of other heterocyclic rings with analgesic activity, the reaction has been extended to 4-quinazolones which have been treated with alkyl or aryl magnesium halides to give the substituted 4-quinazolols :



* II-R = -C₆H₅; III-R = -CH₂.CH₂.CH₃; IV-R = -CH₂.CH₂.CH₂.CH₃

2-Methyl-3-phenyl-4-quinazolinone (I), required for these reactions, was prepared by the method of Grimm, Guenther and Morgan (*J. Amer. Chem. Soc.*, 1946, **68**, 543). It may be mentioned that only very few hydroxy derivatives of quinazolines have so far been reported in literature.

EXPERIMENTAL

2-Methyl-3 : 4-diphenyl-4-quinazolinol (II).—The Grignard reagent was obtained in the usual manner from magnesium (1.2 g., 0.05 mole) and 7.9 g. (0.05 mole) of bromobenzene in 50 c.c. of dry ether in an atmosphere of nitrogen in a three-necked flask, fitted with a dropping funnel, a reflux condenser and a mechanical stirrer. When the magnesium had gone into solution, the flask was cooled in ice and salt and 11.8 g. (0.05 mole) of 2-methyl-3-phenylquinazolinone (I), suspended in 100 c.c. dry benzene, were rapidly added. The ice-bath was removed after 15 minutes and the mixture refluxed for five hours after which it was poured over crushed ice and acidified with dilute hydrochloric acid. The precipitated quinazolinol was collected at the pump, washed with a little cold water, dried and recrystallised from boiling ethyl alcohol in white crystals, m.p. 258-60°, yield 7.5 g. (I) is also soluble in hot water. (Found: N, 9.15. $C_{21}H_{18}ON_2$ requires N, 8.95 per cent).

2-Methyl-3-phenyl-4-n-propyl-4-quinazolinol was obtained as above by the addition of *n*-propylmagnesium bromide (prepared from 0.3 g. magnesium and 1.6 g. *n*-propyl bromide in 25 c.c. dry ether) on 3 g. of the quinazolinone (I), suspended in 30 c.c. of dry benzene. It was recrystallised from boiling ethyl alcohol in white crystals, m.p. 262-65°, yield 2.5 g. (Found: N, 9.6. $C_{18}H_{20}ON_2$ requires N, 10.00 per cent).

2-Methyl-3-phenyl-4-n-butyl-4-quinazolinol was obtained as above by the action of *n*-butylmagnesium bromide (prepared from 0.3 g. magnesium and 1.6 g. of *n*-butyl bromide in 25 c.c. dry ether) on 3 g. of the quinazolinone (I), suspended in 30 c.c. of dry benzene. It was recrystallised from boiling ethyl alcohol, m.p. 272°, yield 2.5 g. (Found: N, 9.21. $C_{18}H_{22}ON_2$ requires N, 9.52 per cent).

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STUDIES ON BASIC SULPHATES OF BIVALENT METALS. PART IV. Be

BY BARUN CHANDRA HALDAR

Thermometric titrations of beryllium sulphate with sodium hydroxide solution and *vice versa* indicate the existence of the basic sulphate $\text{BeSO}_4 \cdot \text{BeO}$.

Beryllium being a bivalent metal is expected to show similarity with other bivalent metals such as Cu, Zn, Cd, etc. In previous papers (Haldar, *J. Indian Chem. Soc.*, 1946, 23, 147, 183) it has been shown by the author that Cu, Zn and Cd give basic sulphates of the type $\text{RSO}_4 \cdot 3\text{RO}$ where R = Cu, Zn or Cd in all concentration ranges and the basic salt $\text{RSO}_4 \cdot \text{RO}$ exists only in concentrated solution. However, at the outset it cannot be said with any certainty about the type of basic beryllium sulphate, although it is expected that either of the type $\text{RSO}_4 \cdot 3\text{RO}$ or $\text{RSO}_4 \cdot \text{RO}$ or both of them will be given by beryllium. This is due to the fact that as a bivalent metal only general similarity with other bivalent metals is expected and it being a typical element, may not show similarity with other bivalent metals in detail. Indications of basic salt, hydroxide and beryllate formations are expected to be observed in the temperature-concentration curves and hence the author has titrated beryllium sulphate with caustic soda solution and *vice versa* by thermometric method. That, beryllium hydroxide dissolves in alkali hydroxide solution naturally suggests a beryllate formation which, however, points to its similarity with Cu and Zn and probably with Cd, which has also been reported to give cadmates. But no indication of cadmate formation has been observed by thermometric method, although in the case of Cu and Zn, distinct indications of cuprate and zincate formations are obtained by this method.

EXPERIMENTAL

The thermometric apparatus is the same as that has been described in a previous paper (Haldar, *loc. cit.*). Reagents used were all of 'Analar' quality. Beryllium was estimated as beryllium oxide.

TABLE I

NaOH solution = 0.4843 M. 40 C. c. of 0.05004 M- BeSO_4 soln. used.

NaOH soln. added	Temp. reading.	Total rise in temp.	NaOH soln. added.	Temp. reading.	Total rise in temp.	NaOH soln. added.	Temp. reading	Total rise in temp
0 c.c.	2.010	0.000	7 c.c.	1.500	0.510	14 c.c.	1.380	0.630
1	1.920	.090	8	1.450	.560	15	1.370	.640
2	1.830	.180	9	1.430	.580	16	1.370	.640
3	1.740	.270	10	1.420	.590	18	1.350	.660
4	1.660	.350	11	1.410	.600	20	1.330	.680
5	1.610	.400	12	1.400	.610	22	1.310	.700
6	1.550	.460	13	1.390	.620	24	1.290	.720

TABLE II

NaOH solution = 0.9686 M. 40 C. c. of 0.1008 M-BeSO₄ soln. used.

NaOH soln.	Temp. reading.	Total rise in temp.	NaOH soln.	Temp. reading.	Total rise in temp.	NaOH soln.	Temp. reading.	Total rise in temp.
0 c.c.	2.570	0.000	4 c.c.	1.960	0.610	8 c.c.	1.630	0.940
1	2.390	.180	5	1.860	.710	9	1.610	.960
2	2.240	.330	6	1.780	.790	10	1.610	.960
3	2.100	.470	7	1.700	.870	11	1.610	.960
						12	1.610	.960

TABLE III

BeSO₄ soln. = 0.5040 M. 40 C. c. of 0.1008M-NaOH soln. used.

BeSO ₄ soln.	Temp. reading.	Total rise in temp.	BeSO ₄ soln.	Temp. reading.	Total rise in temp.	BeSO ₄ soln.	Temp. reading.	Total rise in temp.
0 c.c.	4.520	0.000	4 c.c.	4.100	0.420	8 c.c.	4.065	0.455
1	4.390	.130	5	4.080	.440	9	4.065	.455
2	4.270	.250	6	4.075	.445	10	4.065	.455
3	4.140	.380	7	4.070	.450	11	4.065	.455
						12	4.065	.455

TABLE IV

BeSO₄ soln. = 0.5040 M. 40 C. c. of 0.1262M-NaOH soln. used.

BeSO ₄ soln.	Temp. reading.	Total rise in temp.	BeSO ₄ soln.	Temp. reading.	Total rise in temp.	BeSO ₄ soln.	Temp. reading.	Total rise in temp.
0 c.c.	5.050	0.000	6 c.c.	4.250	0.800	12 c.c.	4.060	0.990
1	4.870	.180	7	4.210	.840	13	4.040	1.010
2	4.700	.350	8	4.170	.880	14	4.020	1.030
3	4.530	.520	9	4.130	.920	15	4.000	1.050
4	4.380	.670	10	4.100	.950	16	3.980	1.070
5	4.280	.770	11	4.080	.970	18	3.940	1.110

DISCUSSION

All the temperature-concentration curves show break at the point beryllium sulphate : caustic soda = 1 : 1. This undoubtedly points to the basic salt formation of the type BeSO₄.BeO. But no indication of the basic salt, BeSO₄.3BeO is observed, although it has been observed in the case of Cu, Zn and Cd. Breaks corresponding to normal hydroxide do not appear exactly at the point BeSO₄ : NaOH = 1 : 2, but 1 : 1.92, when BeSO₄ solutions are titrated with caustic soda solutions. This result is in accordance with that of Britton (*J. Chem. Soc.*, 1925, 2122) who observed electrometrically inflexion in the *p_H*-concentration curves when 1.91 equivalent of alkali was added to BeSO₄ solution. In reverse thermometric titrations *i.e.*, when Be sulphate solution is added to caustic soda solution, change in the straight line curves

takes place at the point $\text{BeSO}_4:\text{NaOH} = 7:16$. This change is probably not due to beryllate formation, for, if this would have been the case,³ it would

FIG. 1

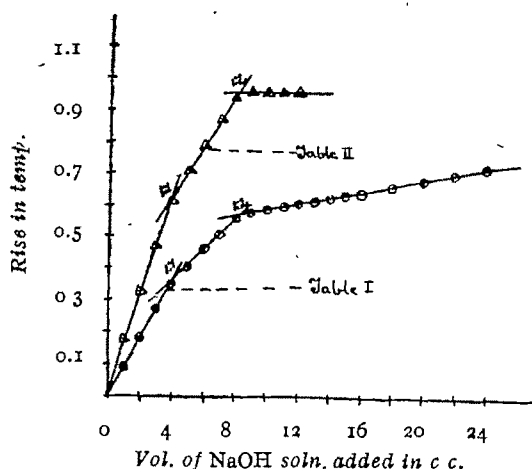
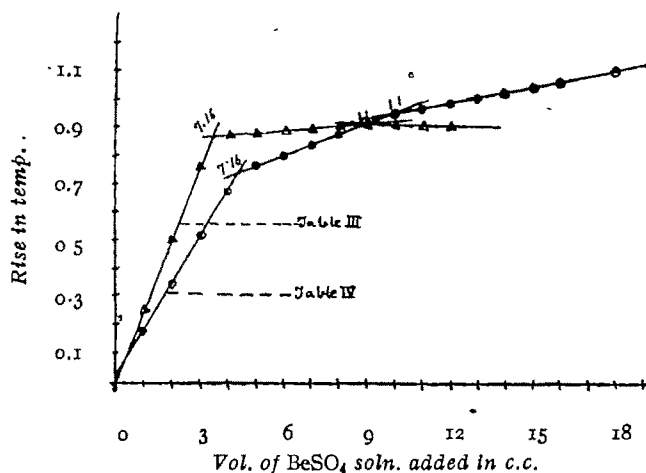
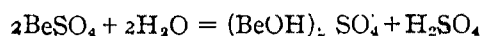


FIG. 2



have been indicated when caustic soda solution was added to BeSO_4 solution. It may be explained as, Be sulphate begins to react with the precipitated Be hydroxide before the precipitation of the hydroxide is complete, to form the stable basic sulphate $\text{BeSO}_4 \cdot \text{BeO}$. Thus although it has been observed by all that Be hydroxide dissolves in alkali hydroxide, no indication of beryllate formation is obtained from thermometric titration curves. The existence of the basic salt $\text{BeSO}_4 \cdot \text{BeO}$ suggests that hydrolysis of Be sulphate in dilute solution should take place according to the equation



or



It has actually been observed that Be sulphate solution is acidic and the hydrolysis in dilute solution takes place according to the above equation. But if one passes from dilute solution to increasingly concentrated solution, it is observed that the behaviour becomes quite different. Dilute solution of Be sulphate can take up 1 mol. of BeO per mol. of Be sulphate in accordance to the above mechanism, but concentrated solution of Be sulphate can take up even two mols. of BeO per mol. of Be sulphate. Again in the case of normal hydrolysis, it is an established fact that hydrolysis increases with dilution. But in concentrated solution of Be sulphate, hydrolysis, as observed from hydrogen ion activity of the solution by Pritz (*Trans. Faraday Soc.*, 1928, **24**, 281), increases with increasing concentration of the salt. Britton's view of colloidal aggregate formation between Be(OH)_2 and BeSO_4 in concentrated solution cannot be supported by experimental evidences, although he, as support to his views, has referred to the observation of Parsons, Robinson and Fuller (*J. Phys. Chem.*, 1907, **11**, 651). It was observed by them that the freezing point of BeSO_4 solution was slightly raised by the addition of the oxide and its conductivity slightly diminished. But it is to be noted that they themselves conclude that the basic solutions are not colloidal, since they cannot be separated by dialysis and are not coagulated by electrolysis. They suggested to explain the oxide dissolving in the salt as camphor dissolves in acetic acid even when it is diluted with water. Sidgewick and Lewis (*J. Chem. Soc.*, 1926, 1287) are, however, of opinion that the oxide combines with the beryllium ion to form a complex cation $[\text{Be}(4\text{BeO})]^{++}$. But this view too presents certain difficulties. If the beryllated ion be of the form as stated above, then it suggests that one mol. of BeSO_4 will dissolve 4 mols of BeO, which is not the case. Secondly, with the above view it is too difficult to explain the high acidity of concentrated BeSO_4 solution. From the solubility measurements Punche and Josien (*Bull. Soc. chim.*, 1940, **7**, 755, 955) have concluded that the basic sulphate $\text{BeSO}_4 \cdot \text{BeO}$ exists only. They have tried to explain the high solubility of beryllium oxide in beryllium sulphate as due to colloidal aggregate formation, although they have not been able to discard the observations of Parsons, Robinson and Fuller (*loc. cit.*). So it is clear that normal hydrolysis of BeSO_4 takes place only in dilute solutions and after a certain concentration, a new type of reaction mechanism takes place. Considering the high acidity of concentrated BeSO_4 solution it is probable that a complex acid of the type $\text{H}_n \left[\text{Be} \begin{array}{c} (\text{OH})_n \\ \text{SO}_4 \end{array} \right]$ exists in the solution and with dilution this passes over to the basic salt $(\text{BeOH})_2\text{SO}_4$ and then the normal hydrolysis proceeds. The nature of the complex acid is, however, to be determined and further investigation is needed for it.

The author's best thanks are due to Prof. P. B. Sarkar, Dr. es. Sc., F.N.I., for his helpful suggestions, keen interest and all laboratory facilities during the progress of the work.

GHOSH PROFESSOR'S LABORATORY,
CHEMISTRY DEPARTMENT,
UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY,
CALCUTTA.

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A NOTE ON THE LIMITS OF SUPERSATURATION AND THE HEAT OF SOLUTION

BY RAM GOPAL

In a series of papers published by the author (this *Journal* 1943, 20, *et seq.*), it has been shown that if $T_s - T$ denotes the degree of supersaturation; λ , the heat of solution of the solute in question; σ , the interfacial tension between the solute and its solution and V_m , the molar volume of the solute, then, in general, $(T_s - T) \lambda$ varies as σV_m . In cases where σV_m values are approximately equal, $(T_s - T) \lambda$ values are also approximately the same. The experimental evidence is summarised in Table I.

TABLE I

Substance.	λ .	$T_s - T$.	$(T_s - T) \lambda$.	Substance.	λ .	$T_s - T$.	$(T_s - T) \lambda$.
KCl	4046	19.6	78897	NaClO ₃	5600	12.0	67200
KBr	5080	16.3	80804	NaCl	1220	51.0	62220
KI	5110	15.5	79205	NH ₄ Cl*	3880	20.0	77600
KBrO ₃	9760	8.8	84788	(NH ₄) ₂ SO ₄ *	2370	24.0	56880
KIO ₃	6780	13.5	91490	NH ₄ NO ₃	6320	10.3	65016
KClO ₃	9950	6.6	65670	HgCl ₂	3300	25.0	82500
KNO ₃	8800	13.0	114400 (?)	CuSO ₄ **	2750	36.7	80925
KClO ₄	12100	6.3	76230	NaClO ₄ **	3600	20.0	72000
KCNS	6100	13.0	79300	NH ₄ ClO ₄ **	6360	12.0	76320
NaNO ₃	5030	13.0	65399	Ba(ClO ₄) ₂ **	9400	9.0	84600

*Not very regular.

**Unpublished yet.

From Table I it is clear that $(T_s - T) \lambda$ is very approximately a constant and the mean value lies in the neighbourhood of 80,000 cal.

The constancy of the expression $(T_s - T) \lambda$ denotes that a solute possessing a higher heat of solution in water has a greater tendency for recrystallisation from aqueous supersaturated solution and *vice versa*. An attempt has been made to explain this result in this communication.

Let us imagine that a solute dissolves in vacuum, then the heat of solution, say λ_v , under these circumstances, will be equal to the lattice energy of the solute in question (cf. Fajans, *Ber. physikal. Ges.*, 1919, 21, 549; Butler, *Z. physikal. Chem.*, 1924, 113, 283). We can now substitute hypothetical solvent 'vacuum' with a real solvent, say water. The heat of the solution, say λ_w , which will now be required for dissolution of the solute, instead of λ_v , should, from an analogy with solution in vacuum, correspond to the lattice energy of the solute when it is kept in contact with the solvent water. The heat of solution, like lattice energy, is a kind of potential energy and part of this latent heat energy, under appropriate conditions, can be converted into mechanical work. One of the possible, and perhaps most probable way, is when the solute crystallises out from

its supersaturated solution. When a nucleus of radius r is formed from a supersaturated solution, the work done is $2M\sigma/\rho r$, M being the molecular weight and ρ , the density of the solute in the solid state. If we consider only such solutes for which $\sigma M/\rho$ or σV_m values are approximately equal, then during the formation of a particle of radius r^* , the same amount of work will be done in all the cases. Hence, those cases in which the crystal (or lattice) forming units have absorbed a higher heat of solution and thus possess a higher potential energy, will have a greater tendency for performing the work $2V_m/r$ i. e. a greater tendency for crystallisation, and therefore a solute possessing a higher heat of solution will, in general, crystallise out with greater ease and *vice versa*.

The above considerations imply that the heat of solution should be inversely proportional to the limit of supersaturation as measured by $T_s - T$. In other words, $(T_s - T)\lambda$ should be a constant and this is, in fact, the experimental result as given in Table I. Thus we see that it is possible to explain the result $(T_s - T)\lambda = \text{a constant}$, if the heat of solution is considered as the lattice energy of the solute when it is kept in contact with the solution.

* The radius of the nucleus formed at first T and various T_s in these substances lies in the neighbourhood of 1×10^{-6} cm. (this *Journal*, 1944, 21, 105; cf. also Davis, *J. Amer. Chem. Soc.*, 1916, 38, 1173; and Harbury, *J. Phys. Chem.*, 1946, 50, 190).

CHEMICAL LABORATORIES,
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STUDIES ON BASIC SULPHATES OF BIVALENT METALS. PART V. NICKEL

BY BARUN CHANDRA HALDAR

The basic sulphate $\text{NiSO}_4 \cdot 3\text{NiO}$ has been found to exist by thermometric method.

Basic sulphates of nickel have not been studied in detail. From its position in the periodic table and its bivalent nature, it is expected to give basic sulphates either of the type $\text{RSO}_4 \cdot 3\text{RO}$ or $\text{RSO}_4 \cdot \text{RO}$ or both, as in the case of other bivalent metals (Cu, Zn, Cd, Be). But literatures on basic sulphates of nickel do not state anything about the existence of the basic sulphate of the type $\text{RSO}_4 \cdot 3\text{RO}$ or $\text{RSO}_4 \cdot \text{RO}$. Moreover, basic sulphates, stated to exist by different workers, do not agree with each other. Athanésco (*Compt. rend.*, 1886, 103, 271) claimed to have crystallised the compound $5\text{SO}_3 \cdot 6\text{NiO} \cdot 4\text{H}_2\text{O}$ where nickel : hydroxide equals to 3:1. According to Pickering (*J. Chem. Soc.*, 1907, 91, 1985) the primary basic salt is $5\text{NiO} \cdot 3\text{SO}_3$ from which two other basic sulphates, namely $5\text{NiO} \cdot 2\text{SO}_3$ and $5\text{NiO} \cdot \text{SO}_3$ are formed successively and the last named one is the most stable. Again Gire (*Compt. rend.*, 1933, 197, 1646) from the hydrolysis of nickel sulphate solution has concluded that the percentage of SO_3 in the basic salt, $\text{NiSO}_4 \cdot 4\text{NiO} \cdot x\text{H}_2\text{O}$ is always less than that required by the above formula, the deficit increasing with washing. Thus, it is quite evident that the results of different workers do not agree with one another and it also appears that the basic sulphates of nickel, if they exist at all, are not very stable. So, in order to study the basic sulphate formation by nickel, it will not be judicious to remove the solid phase from the mother-liquor, because in that case, the solid phase may decompose and indicate the existence of a different compound. The best way to study such unstable systems will be by some physical method where removal of the solid phase from the mother-liquor is not required. The author has studied nickel sulphate-caustic soda system by thermometric method in continuation of his work on studies on basic sulphates of bivalent metals.

EXPERIMENTAL

The thermometric apparatus is the same as that has been described in a previous paper (Haldar, *J. Indian Chem. Soc.*, 1946, 23, 147). Reagents used were all of 'Analar' quality. Nickel was estimated as nickel dimethylglyoxime.

DISCUSSION

The basic sulphate of the type $\text{NiSO}_4 \cdot 3\text{NiO}$ is formed by nickel and is clearly indicated by the sharp breaks in the temperature-concentration curves (Fig. 1). But this change appears only when caustic soda solution is added to nickel sulphate solution. In the reverse case i.e., when nickel sulphate solution is added to caustic soda solution no such breaks appear. This is due to the fact that nickel hydroxide, formation of which is indicated in all the cases, once formed, does not pass on to the basic sulphate

$\text{NiSO}_4 \cdot 3\text{NiO}$ by reacting with further quantity of nickel sulphate and the basic sulphate $\text{NiSO}_4 \cdot 3\text{NiO}$ is probably stable only in presence of excess of nickel sulphate. It is peculiar that no indication of any other basic sulphate formation, as reported by various workers previously, are obtained by the thermometric method.

FIG. 1

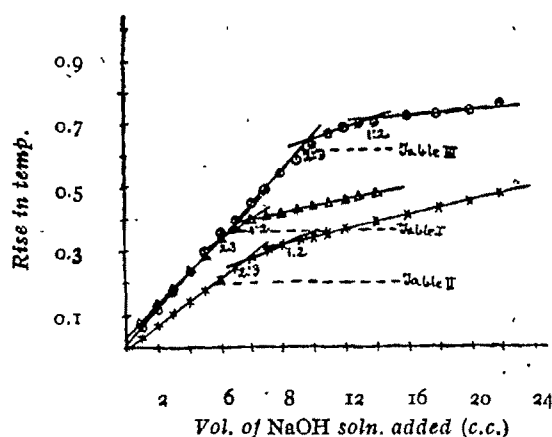


FIG. 2

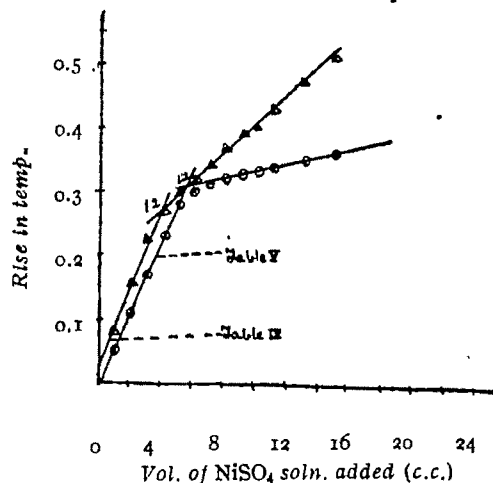


TABLE I

40 C. c. of 0.10590M-nickel sulphate soln. used NaOH soln. = 1.059 M.

NaOH soln. added	Temp. reading	Total rise in temp.
0 c. c.	4.140	0.000
1	4.080	.060
2	4.010	.130
3	3.960	.180
4	3.900	.240
5	3.850	.290
6	3.800	.340
7	3.765	.375
8	3.740	.400
9	3.730	.410
10	3.720	.420
11	3.710	.430
12	3.700	.440
13	3.690	.450
14	3.680	.460
15	3.670	.470
16	3.660	.480

TABLE II

40 C. c. of 0.06445M-nickel sulphate soln. used NaOH soln. = 0.5156 M.

NaOH soln. added	Temp. reading	Total rise in temp.
0 c. c.	3.820	0.000
1	3.790	.030
2	3.750	.070
3	3.720	.100
4	3.680	.140
5	3.640	.180
6	3.610	.210
7	3.570	.250
8	3.540	.280
9	3.520	.300
10	3.500	.320
11	3.490	.330
12	3.480	.340
13	3.465	.355
14	3.455	.365
16	3.430	.390
18	3.410	.410
20	3.390	.430
22	3.370	.450
24	3.350	.470

TABLE III

40 C. c. of 0.20375M-nickel sulphate soln. used NaOH soln. = 1.0594 M.

NaOH soln. added	Temp. reading	Total rise in temp.
0 c. c.	3.440	0.000
1	3.380	.060
2	3.320	.120
3	3.260	.180
4	3.200	.240
5	3.140	.300
6	3.080	.360
7	3.040	.400
8	2.990	.450
9	2.950	.490
10	2.900	.540
11	2.850	.590
12	2.805	.635
13	2.770	.670
14	2.750	.690
15	2.740	.700
16	2.740	.700
18	2.720	.720
20	2.710	.730
22	2.700	.740

TABLE IV

40 C. c. of 0.1262M-NaOH soln. nickel
sulphate soln. = 0.6445 M.

Ni sulphate soln.	Temp. reading.	Total rise in temp.
0 C. c.	4.870	0.000
1	4.790	.080
2	4.710	.160
3	4.640	.230
4	4.600	.270
5	4.570	.300
6	4.550	.320
7	4.530	.340
8	4.500	.370
9	4.480	.390
10	4.470	.400
11	4.440	.430
12	4.420	.450
13	4.400	.470
14	4.380	.490
15	4.360	.510
16	4.340	.530
17	4.320	.550
18	4.300	.570

TABLE V

40 c. c. of 0.1710M-NaOH soln. nickel
sulphate solution = 0.6445M.

Ni sulphate soln.	Temp. reading.	Total rise in temp.
0 C. c.	3.500	0.000
1	3.450	.050
2	3.390	.110
3	3.330	.170
4	3.270	.230
5	3.220	.280
6	3.200	.300
7	3.190	.310
8	3.180	.320
9	3.170	.330
10	3.170	.330
11	3.160	.340
13	3.150	.350
15	3.140	.360

The author's best thanks are due to Prof. P. B. Sarkar, Dr. é.s. Sc., F. N. I. for his keen interest, helpful suggestions and all laboratory facilities during the progress of the work.

GHOSH PROFESSOR'S LABORATORY,
CHEMISTRY DEPARTMENT,
UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY,
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ROLE OF SCIENTISTS IN THE CONTROL OF ATOMIC ENERGY

In our last issue we have published the reply, which the Council of the Indian Chemical Society gave to the letter of the Committee for Foreign Correspondence of the Federation of American Scientists inviting the views and opinions of the Indian Chemical Society on the subject of international control of atomic energy and atomic armament race. In view of the paramount importance of the subject we make no apology to revert to it again for a further elaboration of the salient points referred to in that reply.

The Council of the Indian Chemical Society has rightly indicated that the responsibility of the scientists in the matter is possibly far greater than that of any other public body, if only because of the fact that it was the scientists who, deluded by the so-called spirit of nationalism and loyalty to the state, and, it may also be added here, lured to a certain extent by highly profitable salaries and rewards, co-operated in the production of such marvels of technological skill in the form of tanks, rock-bursters, V-weapons, rocket-bombs, flame-throwers and atomic bombs. While engaged in the production of these deadly instruments of mass-slaughter they allowed their scientific judgment to be clouded by a false pride of victory in the cause of humanity. The humanity is now groaning under the crushing weight of their own inventions. They cannot, therefore, escape their share of the guilt of the scientifically planned indiscriminate mass massacre and wholesale destruction of the last two global wars, which have landed the world to-day in a state of utter moral and material chaos with scarcity and starvation for millions. Besides, scientists in general have also contributed indirectly in no less measure to the creation of a mental climate or ideologies, full of potentialities for human conflicts, by advancing a materialistic theory of life and human progress. The philosophical foundation and background of the sciences, which generally account for their limitations, were clearly understood only by a very few. As a result, a simplified picture of the world and reality emerged out of the scientific progress and was universally accepted with an almost fanatical faith. This has gradually led to a denial of human personality and human values. All moral values have been branded as illusions, worthy only of sick-brained visionaries; spirituality has been explained as a perverted or misdirected sex-instinct. Human beings are believed as nothing better than animals or machines made of flesh and blood, controlled by mechanical laws of physics and chemistry. And all this pass current in the name of progress. Thus the scientists have produced, the political rulers have enjoined, and the rank and file have used all the dreadful new weapons and complicated gadgets of war with the least qualm of conscience for the perpetration of such dastardly outrages like area bombing and saturation bombing under the conviction that they are acting for the good and progress of humanity.

Unfortunately, this so-called scientific picture of the world and reality still persists in the mind of many, not excluding a large body of the scientists themselves. The enormity of the unprecedented catastrophes of the last world war has failed to awaken the people at large, and with the return of an uneasy peace of scarcity and starvation they have engaged themselves once again in activities, effective only for perpetuating the causes of war. The world has thus learned nothing. Indeed, it has been said that the most important lesson of history is that

nobody ever learns history's lessons. It is alleged that in America a large body of experts, including many Nazi scientists, are engaged to-day in extensive researches for war purposes, which cover land and air arms, submarines and naval surface craft, atomic chemical and bacteriological weapons. In fact, science and technology are being militarized and misapplied for the purpose of destruction. If there be any truth in these reports, the Federation of American Scientists has much work to do nearer home. And it is very likely that from this realization they have just dissolved their Committee for Foreign Correspondence.

In their reply the Council of the Indian Chemical Society has rightly emphasized the pressing need for the scientists to organize and educate the members of their own profession than launching a wider campaign for enlightening the public opinion of the world, the right for which they will forfeit if they fail to keep their own house in order.

Hence, in this matter of atomic energy control the action of the scientists may profitably follow two main directions as indicated below.

Nationalism, as it stands to-day, aims neither at liberty nor safety, nor even lasting prosperity, for the individual. So we find the common man in every nation to-day is faced either with material or moral ruin. Applied science in the service of nationalism has wrought this havoc. What is most needed, therefore, is a reorientation of applied science and its utilization for serving the fundamental human needs and forwarding the causes of human welfare, human safety and human liberty. Instead of researches on the discovery of increasingly more destructive armaments and ammunitions of war, scientists and technicians should devote their attention to the increased production of food, the discovery of more effective medicines, biological researches in general, and the production of cheap power that might be utilized equally by all to meet their primary requirements.

Finally, scientists can organize themselves into an international federation and refuse on conscientious grounds to lend their service or advice for any work connected with preparations of war, or with exploitations and enslavement of human beings. This non-cooperation with evils has been particularly stressed upon by the Council of the Indian Chemical Society in their reply, referred to. For this, of course, the scientists will have to prepare themselves for all possible persecutions and sacrifices. It endorses, in fact, the suggestion made by Dr. Gene Weltfish in one of the issues of the *Scientific Monthly* of 1945. Scientists and technicians, while enlisting themselves as members of such an international federation, should take an oath, in the words of Dr. Weltfish, as follows :

"I pledge myself that I will use my knowledge for the good of humanity and against the destructive forces of the world and the ruthless intent of men, and that I will work together with my fellow scientists of whatever nation creed or colour for these our common ends."

PERFORMANCE OF SIEVE PLATE FRACTIONATING COLUMNS.
PART I. EFFECT OF DISTILLATION RATE
AND CONCENTRATION

BY S. K. NANDI AND B. KARIM

CHEMICAL ENGINEERING LABORATORIES, INDIAN INSTITUTE OF SCIENCE, BANGALORE

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The effect of distillation rate and concentration on the performance of a sieve plate fractionating column has been studied with four binary mixtures: water-ethyl alcohol, water-methyl alcohol, water-acetone and toluene- CCl_4 . A 2½" diameter glass column with six plates and a similar metal column, with arrangements for taking liquid and vapour samples from each plate have been used for the purpose. Column efficiency is expressed as overall plate efficiency and individual Murphree plate efficiency. Maximum efficiency has been obtained only when the rate of distillation is within a certain range, above and below which the efficiency drops down rapidly. Concentration of the feed mixture has practically no effect on column efficiency. Under optimum conditions very high efficiencies, above 100%, are obtained.

The performance of different types of fractionating columns has received a considerable amount of investigation by chemical engineers and the progress made in recent years is remarkable. Superfractionating columns¹ containing as many as 150 plates or more with reflux ratio of 100 to 1 and with temperature control within 1 to 2°F are now used in industries. Colossal fractionating columns were constructed during the last war for the manufacture of synthetic rubber and atom bomb.

Although a large amount of work has been done on the performance of bubble cap and packed columns, data on the performance of sieve plate columns, both of industrial and laboratory type, are very few. The efficiencies of sieve plate columns, as reported in the literature, are usually much lower than those of bubble cap columns. In the present investigation the effects of the design and operation variables on the performance of a sieve plate column have been studied with a view to finding out the factors which would give higher efficiency.

The distillation unit (Fig. 1) was designed to study rectification under total reflux at atmospheric pressure. A 11-litre copper vessel with provision for introducing and taking out liquid constitutes the still or reboiler, S. A 2000 watt electric immersion heater, connected in series with an ammeter and adjustable rheostat is used to heat the liquid contained in the still. The glass manometer (M) gives an indication of the pressure drop and also of the level of the liquid in the still. The column, C is fitted to the top of the still by flanged joint. In the preliminary investigations a glass column was used,

the construction of which presented considerable difficulty because of non-availability of flanged glass pipes. The column was constructed by fixing 5' long bits of pyrex glass tube of $2\frac{1}{4}$ " internal diameter to metal pieces by means of gland nut. Six sieve plates and vapour and liquid samplers were fixed to the metal pieces and the general method of assembly to make the whole system

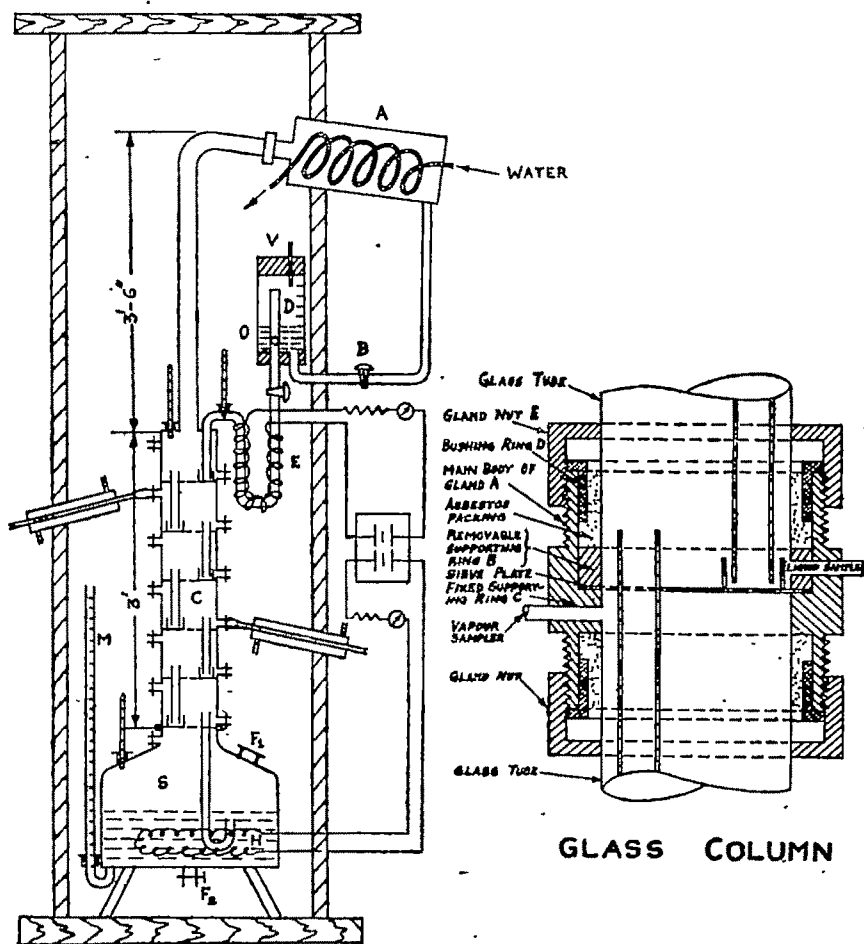


FIG. 1. Laboratory sieve plate fractionating column.

leak-proof will be clearly seen from Fig. 1. Iron clamps were welded in each metal gland and fixed to a 10' high stand running on both sides of the column. Because it was difficult to change the design of the glass column very frequently a similar metal column was constructed by assembling flanged copper tubes. The two distillation equipments—one with glass column and the other with metal column—were kept side by side. In the preliminary investigations the glass column was used for facilitating visual observation and the results were later on confirmed in the metal column.

The perforated plates, downpipes, sealing cups for downpipes were all made of copper. The entire distillation unit was lagged with coconut coir and 85% magnesia. In the glass column the glass portions were covered with cotton wool and not with magnesia so that visual observations could be made whenever desired by removing the cotton wool. Some of the details of the column are as follows :—

Height of column = 3 ft.	$\frac{\text{Area of downpipe}}{\text{Area of plate}} = 3.16\%$	$\frac{\text{Total area of holes}}{\text{Area of plate}} = 1.981\%$
Diameter = $2\frac{1}{2}$ inch.		
Internal diameter of	No. of plates = 8	Plate spacing = 6 inch
downpipe = $2\frac{5}{8}$ inch.	No. of holes per plate = 100	Submergence = 1 inch
	Diameter of holes = $1/32''$	

Operation

The vapour coming from the still, after being condensed in the condenser, was passed through the 3-way stop-cock B to the flowmeter, D and then back to the column after being heated in the electrically heated U-tube reflux heater, E. Heating in the reflux heater was so adjusted that the reflux indicated a temperature of 3° to 5°F below the temperature of the top of the column. Reflux was introduced on the sealing cup of the top plate. The flowmeter used was of the submerged orifice type and was calibrated at different flow rates. In each run, the rate of distillation was measured not only by the flowmeter but was also checked by direct measurement. It took about 2 to 4 hours for the column to attain equilibrium, as indicated by the constant temperature shown by the thermometers on the reboiler, column top and reflux inlet line.

When equilibrium was established, samples of vapour and liquid were withdrawn very slowly from each plate, making certain that the plates were not drained. Sampling was started from the top plate and an interval of a few minutes was allowed between successive samples. It took about 2 hours to collect all the samples. The liquid and vapour samples were passed through a condenser before they were collected in sampling bottles.

The following binary mixtures were studied in the present investigation :—
 (1) Ethyl alcohol-water, (2) methyl alcohol-water, (3) acetone-water, (4) toluene-carbon tetrachloride.

Analysis of these mixtures was made by the density determination. For methyl alcohol-water and ethyl alcohol-water data given by Perry² and for acetone-water, data of Squibb³ were used. Analysis of acetone-water mixtures was occasionally checked by Messinger's method⁴. The results obtained by the two methods were found to agree remarkably well. Toluene— CCl_4 mixture was analysed both by density (data taken from Chemical Engineering laboratory Equipments by Zimmerman & Lavine, 1943) and by

refractive index (data from International Critical Tables) determinations. The density was determined by a pycnometer and the refractive index by a Pulfrich refractometer.

Equilibrium data for the systems were taken from the latest literature. For ethyl alcohol-water, methyl alcohol-water and toluene-carbon tetrachloride data given by Perry² and for acetone-water, data of Othmer⁵ were used.

The number of the theoretical plates was calculated for all the systems by the graphical method of McCabe and Thiele⁶ with the equilibrium curve drawn on a big scale. For the system, toluene-carbon tetrachloride, which obeyed Raoult's law, the number of theoretical plates was also calculated by Fenske equation⁷ for total reflux and the graphical and algebraic methods closely agreed.

EXPERIMENTAL

In studying the effect of a variable the overall efficiency, plate to plate liquid and vapour composition and Murphree efficiencies^{1,6} of different plates were calculated.

Effect of Distillation Rate on Overall Efficiency

In Table I, the overall plate efficiencies with different distillation rates for the different mixtures are given. In the system ethyl alcohol-water, vapour leaving the 2nd plate from top was taken as the product and the vapour coming from below to the 5th plate was taken as the feed and thus the overall plate efficiency of 4 plates (plates 2, 3, 4 and 5) was studied. In the other systems, the liquid from the condenser was taken as the product and the vapour rising from the still was taken as the feed and thus the overall efficiency of 6 plates was determined.

The results are plotted graphically in Fig. 2.

The maximum efficiency appears to be obtained only when the distillation rate is within a certain range. Above and below this range the efficiency drops down rapidly. This is naturally to be expected in a sieve plate column which is not flexible in its operation. It could be visually observed in the glass column that at vapour velocities, too low to maintain the proper liquid head on the plates, drops of liquid were falling through the perforations of the plate making the plate dry in the extreme case and at high velocities there was flooding on some of the plates and the liquid went on accumulating in those plates giving rise to increased entrainment with the result that low efficiencies were obtained. When the velocity was further increased, the liquid accumulated on all the plates,

TABLE I

Run No.	Distillation rate (c.c./min.).	Feed composition (mol. %).	Product composition (mol. %).	No. of theoretical plates.	No. of actual plates.	Overall % efficiency %
System: Ethyl alcohol—water.						
1	15	21.81	77.67	4.18	4	104
2	16	38.96	79.14	4.10	4	102
3	18	44.32	81.25	5	4	125
4	24	34.15	80.45	5	4	125
5	26	20.01	78.37	4.54	4	118
6	28	51.83	79.95	4	4	100
7	31	55.18	80.00	4	4	100
8	36	48.52	76.5	3	4	75
9	43	51.62	77.00	3	4	75
System: Methyl alcohol—water.						
10	10	20.18	99.15	5.7	6	95
11	16	20.25	99.17	5.71	6	95
12	18	21.00	99.17	5.71	6	95
13	20	20.00	97.10	4.0	6	66
14	24	20.01	88.5	2.72	6	45
System: Acetone—water.						
15	16	40.00	97.83	7.41	6	123
16	20	41.00	95.00	3.54	6	59
17	25	45.00	92.00	2.4	6	40
18	30	40.00	90.00	1.66	6	28
System: Carbon tetrachloride—toluene.						
19	10	20.01	97.70	6.01	6	100
20	15	20.05	99.01	7.00	6	116
21	20	20.10	99.75	8.00	6	138
22	25	20.50	96.01	5.01	6	83
23	30	20.60	89.10	4.08	6	67
24	48	21.01	66.00	2.5	6	41

was carried over to the top of the column, leaving the plates completely dry. At this stage the pressure, indicated by the manometer attached to the reboiler, suddenly indicated a 2 or 3-fold rise. The liquid after being carried to the top of the column would not come down but remained there by circulating in a closed cycle through the condenser. On this column, having $1/32''$ holes in the plates, flooding velocities were reached very easily but on plates having $1/16''$ dia. or $1/8''$ dia. holes, studied later on, flooding velocities could not be reached and this tendency of the liquid being carried over from the plates to the top of the column was not observed.

According to Carey, Griswold, Lewis and McAdams⁸, Sherwood and Jenny⁹, Peavy and Baker¹⁰, Gadwa¹¹, Brown and Lockhart¹² and other workers, the mechanism of contact between liquid and vapour in a rectification column changes with the vapour velocity. At high velocities there is formation of foam or froth above the liquid surfaces, increased submergence, better agitation, better liquid-vapour contact, whereas at low velocities these are absent. Two opposing factors come into operation as the vapour velocity is increased. Due to foaming and frothing the contact between liquid and vapour is more perfect, but at the same time there is an increase in entrainment. So long as the gain in concentration due to better contact between the liquid and vapour more than counterbalances the loss by entrainment, the efficiency increases with increase in vapour velocity. But when the reverse happens, the efficiency decreases. Sonders and collaborators¹³ report that for laboratory columns, at the critical loading point, the pressure drop increases three-fold or more, which has also been observed in the present investigation.

Effect of Distillation Rates on Murphree Plate Efficiency

Table II gives the Murphree efficiency of a particular plate with change in vapour velocity. For the system ethyl alcohol-water, the 5th plate from the top, and for the system methyl alcohol-water, the 2nd plate from the top were studied. These readings were taken under identical conditions as those of Table I. The significance of the different symbols used in the following tables are :—

$V_1, V_2, V_3, \dots, V_7$ are compositions of the vapour rising from plates 1, 2, 3 etc. and from the still.

L_1, L_2, L_3, \dots are the compositions of the liquid leaving plates 1, 2, 3, etc.

$V_1^*, V_2^*, V_3^*, \dots$ are the compositions of the vapour in equilibrium with the liquid leaving plates 1, 2, 3, etc.

Em_1, Em_2, Em_3, \dots are the Murphree efficiencies of plates 1, 2, 3, etc.

Plates have always been numbered from the top.

TABLE II

Composition (mol. %)

Distillation rate (c.c./min.).	V ₁ .	L ₁ .	V ₂ .*	V ₃ .	Em ₁ %.
System : Ethyl alcohol—water.					
14	56.38	30.25	57.35	21.81	97.2
16	63.79	43.11	62.44	38.96	105.7
18	67.46	52.91	66.41	44.32	104.7
24	66.73	42.84	62.26	34.15	116
26	59.79	20.64	53.19	20.01	120
28	67.79	49.04	64.81	51.83	123
31	66.44	52.05	66.02	55.18	103.8
36	56.53	37.54	60.27	48.52	68
43	59.84	45.26	63.33	51.62	70
System : Methyl alcohol—water.					
	V ₂ .	L ₂ .	V ₂ *.	V ₃ .	Em ₂ %.
16	97.40	91.98	97.22	91.89	103
24	65.00	40.00	73.00	41.1	75

TABLE III

	System : Ethyl Alcohol—water.				System : MeOH—water.
	Distillation rate (c.c./min.)				
	16.	24.	26.	30.	18.
V ₁					99.15
L ₁					96.51
V ₂	79.14	81.26	76.77	65.26	97.40
L ₂	75.65	81.08	73.80	52.53	91.98
V ₃	75.80	78.08	75.82	50.15	91.89
L ₃	71.54	73.80	63.76	43.74	82.19
V ₄	72.91	74.68	70.52	51.20	77.59
L ₄	65.35	67.68	52.25	38.96	56.76
V ₅	63.79	67.68	48.74	30.80	57.95
L ₅	43.11	50.67	8.61	26.15	18.67
V ₆	38.96	57.10	9.04	30.83	46.80
L ₆					8.4
V ₇					20.18
Em ₁					124.1
Em ₂	110.6	71.1	52.8	85.1	103.4
Em ₃	87.6	115.8	129.5	104.7	88.2
Em ₄	104.3	112.0	125.0	85.2	72.88
Em ₅	105.7	126.0	121.5	24.0	73.35
Em ₆					127.8

It will be seen that Murphree plate efficiency also has maximum value for a certain range of vapour velocity but it decreases rapidly when the velocities are above or below the optimum velocity.

Plate to Plate Liquid and Vapour Composition and Murphree Plate Efficiency

Table III gives the Murphree efficiency and the liquid and vapour composition of each plate.

The composition of the liquid and vapour decreases gradually from the top plate to the bottom plate. Murphree efficiency is different in different plates and varies widely. In a distillation operation, Murphree efficiency of one plate is usually different from that of the other as will be evident from the works of previous investigators¹⁴.

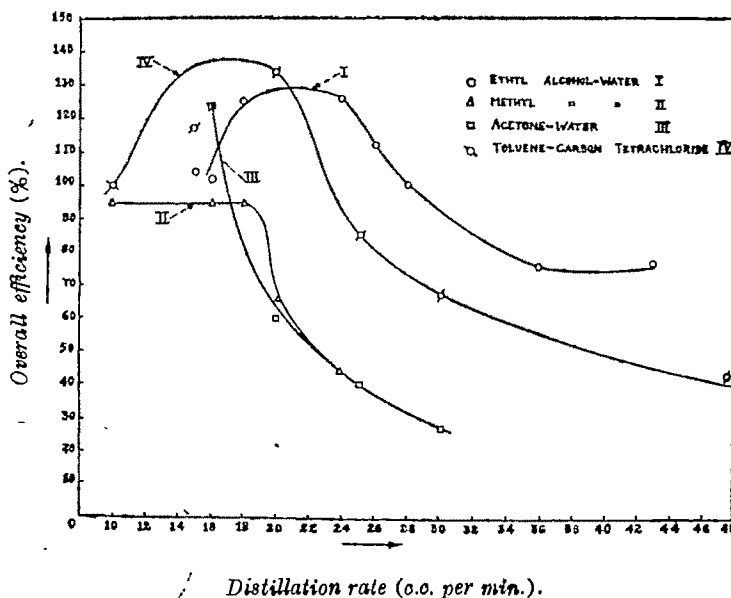


FIG. 2 Distillation rate vs. overall efficiency.

Effect of Concentration on Efficiency

The feed concentration was varied keeping other factors constant and the results obtained are given in Table IV.

It will be seen that the feed concentration does not seem to have any appreciable effect on overall efficiency or Murphree plate efficiency. This observation agrees with the findings of Peavy and Baker¹⁶ and Carey⁹ who found column efficiency to be independent of concentrations even when varying within a wide range for the systems ethyl alcohol-water and benzene-toluene.

TABLE IV

System : Ethyl alcohol—water.

Overall efficiency.					
Reflux rate (c.c./min.).	Composition (mol.%).		No. of, theoretical plates.	No. of, actual plates.	Overall %efficiency.
	Feed.	Product.			
18	21.81	77.67	4.08	4	102
16	38.90	79.14	4.14	4	103
26	9.04	76.77	4.5	4	112
26	20.01	78.87	4.53	4	113
Murphree efficiency.					
Composition (mol %)					
	V _s	L _s	V _s *	V _s	Em%.
24	67.76	52.69	66.81	56.25	114.4
24	72.13	62.89	71.14	64.49	114.9
26	48.74	8.61	41.71	9.04	131.5
26	59.79	20.64	53.19	20.01	120

It will be seen that (a) different binary mixtures give different efficiencies on the same column, and (b) efficiencies above 100% are obtained. These points will be dealt with later on in the general discussions which will follow after the results have been confirmed in all the different types of columns used in this investigation.

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PERFORMANCE OF SIEVE PLATE FRACTIONATING COLUMNS. PART II. EFFECT OF AREA AND SIZE OF PERFORATION

BY B. KARIM AND S. K. NANDI

CHEMICAL ENGINEERING LABORATORIES, INDIAN INSTITUTE OF SCIENCE, BANGALORE

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The effect of area and size of perforations on the performance of a sieve plate fractionating column has been studied with the systems: ethyl alcohol-water, methyl alcohol-water and acetone-water. It has been found that increasing the area of perforations does not alter the efficiency of the column but size of perforations has a remarkable effect on column efficiency. Very high overall efficiencies have been obtained.

The effect of vapour velocity and concentration on the efficiency of a sieve plate column is reported in Part I (this *issue*, p. 3). In the present investigation the same $2\frac{1}{4}$ inch diameter distillation column has been used and the effect of area and size of perforations on column performance are given.

Area of perforations.—The area of perforations in each plate was varied (as follows), keeping the size of holes constant.

(a) 100 holes, $1/82''$ in each plate (Column I)	$\frac{\text{Area of perforations}}{\text{Area of plate}}$	= 1.931%
(b) 200 holes, $1/32''$ in each plate (Column II)	"	= 3.862%
(c) 800 holes, $1/32''$ in each plate (Column III)	"	= 5.793%

The columns consisted of 6 plates with 6" plate spacing and 1" submergence. Three systems, ethyl alcohol—water, methyl alcohol—water and acetone—water were tried in these columns.

Effect of area of perforations on overall efficiency.—Table I shows the results obtained.

In some cases, the liquid sample was taken from the bottom of the still, thus making the number of actual plates 7. It will be seen that so long as the size of holes remains the same, increasing the area of perforations does not have any appreciable effect on the efficiency of the column. In this particular case, the size of holes is very small, $1/32''$, so that even with 300 holes, the ratio of hole area to plate area comes to only 5.793%, as against 10-12% in industrial sieve plate columns. It is very likely that the column efficiency will be affected by increasing the number of holes if the total area of perforations exceeds 10-12% of the area of the plates.

TABLE I

No. of holes per plate.	Run No.	Reflux rate (c.c./min.).	Feed com- position (mol. %).	Product composition (mol. %).	No. of theoretical plates.	No. of actual plates.	Overall efficiency (%)
100 (Column I) Hole area = 1.931 % of plate area.							
Results for systems ethyl alcohol-water, methyl alcohol-water, acetone-water reported in Part I.							
System : Ethyl alcohol—water.							
200 (Column II)	1	10	9.04	81.00	6.17	6	108
Hole area =	2	18	9.01	82.56	7.20	6	120
3.862 %	3	20	9.05	82.56	7.20	6	120
	4	25	11.5	78.20	4.8	6	80
System : Methyl alcohol—water.							
	5	15	20.28	99.16	5.6	6	96
	6	20	21.50	97.20	4.0	6	60
	7	25	20.28	89.5	2.74	6	45
System : Acetone—water.							
	8	18	66.8	98.1	7.3	6	121
	9	24	65.0	96.25	4.2	6	70
System : Ethyl alcohol—water.							
300 (Column III)	10	24.5	2.2	83.23	8.63	7	123
Hole area =	11	28	2.4	82.19	7.63	7	109
5.793 %.	12	30	2.4	80.25	6.0	7	85
	13	32	2.4	75.00	4.9	7	70
	14	70	2.4	61.51	2.8	7	40
System : Methyl alcohol—water.							
	15	11.5	2.0	98.3	6.0	7	85
	16	16.0	3.0	99.15	6.85	7	98
	17	21.0	2.0	97.6	5.9	7	84
	18	25.0	2.0	95.0	4.75	7	68
	19	70.0	1.80	70.05	3.0	7	43
System : Acetone—water.							
	20	16.0	67.0	97.9	7.0	6	116
	21	20.0	67.0	97.0	5.12	6	85
	22	25.0	66.9	95.0	3.14	6	52
	23	30.0	66.9	94.0	2.5	6	41
	24	70.0	67.0	90.0	1.2	6	20

Murphree efficiencies of a single plate of these columns with different vapour velocities for the system ethyl alcohol-water are given in Table II and plate to plate liquid and vapour compositions are given in Table III.

TABLE II
System : Ethyl alcohol-water.

Column details.	Reflux rate (c.c./min.).	Composition (mol. %)				
		\bar{V}_g .	L_g .	V_g^*	V_o .	$Em_g\%$
Column No II, 200 holes	10	64.00	43.15	62.50	42.15	107
	20	67.50	53.00	63.40	45.50	123
	25	66.73	43.00	62.50	36.00	116
Column No. III, 300 holes		V_3 .	L_3 .	V_3^* .	V_4 .	$Em_3\%$
	25	76.84	72.38	76.70	72.98	103

TABLE III
Column III, 300 holes, 1/32" dia., 6 plates, 6" plate spacing.
Reflux rate (c.c/min)

	30. EtOH-water.	23. MeOH-water.	18. Acetone-water.
V_1	80.71	97.79	97.55
L_1	77.89	96.58	97.0
V_2	78.60	95.48	93.75
L_2	76.84	84.01	80.0
V_3	76.84	85.04	60.5
L_3	72.38	60.7	
V_4	72.98	71.48	
Em_1	121.2	75.0	101.0
Em_2	63.8	128.0	112.7
Em_3	102.6	121.5	

Size of perforations.—In order to determine the effect of hole size on column efficiency, different binary mixtures were studied using the following different types of plates :—

(a) 300 holes, 1/32" in each plate (Column III)	Area of holes Area of plate	=5.793%
(b) 75 holes, 1/16" in each plate (Column IV)	"	=5.793%
(c) 19 holes, 1/8" in each plate (Column V)	"	=5.793%

Effect of hole-size on efficiency.—The overall efficiencies are given in Table IV and in Fig. 1.

TABLE IV

Size of holes.	No. of holes.	Run No	Reflux rate (c.c./min.).	Feed composition (mol. %).	Product composition (mol. %).	Theoretical No. of plates	Actual No. of plates.	Overall efficiency (%).
Column III, 1/32" dia. holes	300	For systems ethyl alcohol-water, methyl alcohol-water, acetone-water please refer to Table I runs 10-24						
Column IV, 1/16" dia. holes	75	System : Ethyl alcohol—water.						
		1	20	14.36	80.04	5.45	6	90.8
		2	25	14.32	82.44	6.9	6	115.0
		3	26	14.36	81.81	6.76	6	112
		4	27	14.36	81.81	6.76	6	112
		5	35	14.32	77.89	4.7	6	78
		6	36	14.31	76.72	3.87	6	64
		7	60	14.31	50.89	1.16	6	19
		8	70	14.38	54.00	1.41	6	23
		System : Methyl alcohol—water.						
		9	10	20.17	97.81	4.2	6	70
Do		10	12	20.19	97.81	4.2	6	70
		11	30	20.15	97.40	4.4	6	73
		12	38	20.17	92.75	3.3	6	55
		13	50	20.20	83.00	2.1	6	35
		14	70	20.12	77.40	1.75	6	29
		System : Acetone—water.						
		15	16	5.0	86.0	2.0	6	33
Do		16	20	5.0	83.0	1.81	6	31
		17	25	5.1	80.01	1.73	6	29
		18	30	5.2	70.02	1.3	6	21
		19	50	5.0	64.02	1.0	6	17
		20	60	5.1	60.04	1.0	6	17
		System : Ethyl alcohol—water.						
Column V, 1/8" dia. holes	18	21	30	15.01	72.95	3.25	6	54
		22	54	15.02	81.81	6.5	6	108
		23	60	15.00	79.82	5.25	6	87

The results show that other factors remaining constant, the smaller the perforations, the greater is the efficiency with decreased capacity and *vice versa*. With holes of $1/32''$ diameter very high efficiencies are recorded for all the mixtures varying from 95% in the case of methyl alcohol-water system to 125% in the case of ethyl alcohol-water. As the hole size is increased to $1/16''$ and $1/8''$, the efficiency falls off very rapidly in the cases of methyl alcohol-water and acetone-water, but gradually in the case of ethyl alcohol-water. On the other hand, at higher vapour velocities for the same distillation rate, the efficiency obtained on plates having bigger holes is higher than the corresponding efficiency obtained with smaller sized holes.

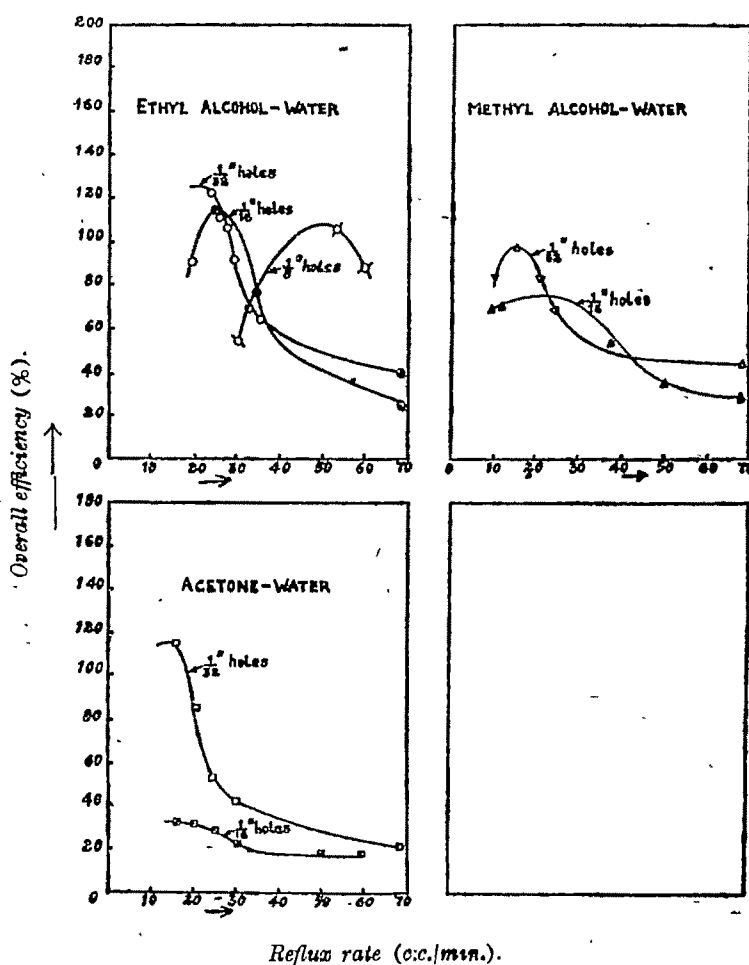


FIG. 1. Hole size vs plate efficiency.

The capacity of a column on the other hand is less in case of plates having $1/32''$ dia. perforations than in the case of plates having $1/16''$ dia perforations due to the fact that the resistance, met by the vapour stream in passing

through 300 $1/32''$ dia. holes, is greater than the resistance encountered by the same amount of vapour in passing through 75 $1/16''$ dia. holes. As a result, the capacity naturally increases with greater hole-size which permits of higher vapour velocity without undue increase of internal pressure.

The increased efficiency in the case of smaller holes is due to the following reasons :—

(a) Firstly, the smaller the hole-size, the finer are the bubbles formed by the vapour stream while passing through the perforations. This provides increased surface of contact between the liquid and vapour and thereby facilitates the transfer of material by counter-current diffusion.

(b) Secondly, the smaller the holes, the easier it is for the vapour stream from below to maintain the liquid on the plate. As the hole-size is increased, greater vapour velocity is required to maintain the liquid on the plate. But greater vapour velocity means more chance of loss of efficiency due to entrainment. Again, if the velocity is too low, the liquid from the plate above will trickle down on the plate below through the holes instead of the overflow pipe which also drastically cuts down efficiency.

The importance of the size of slots in the design of bubble cap columns has been stressed by Carey¹. Using the system ethanol-water he obtained efficiencies of 66%, 70%, 76% and 86% with $\frac{1}{2}''$, $\frac{1}{4}''$, $\frac{1}{8}''$ and $\frac{1}{16}''$ slots respectively. The efficiencies of sieve plate columns reported in literature are rather low compared to the performance of bubble cap columns. Brown² however, reports an overall efficiency as high as 120% for a perforated plate beer still but the working or design data are not given. Gunness and Baker³ working on a beer still with $\frac{1}{8}''$ dia. holes obtained an overall efficiency of 40 to 43%. Peters⁴ obtained 50% efficiency for acetic acid-water mixture on plates having 0.2 inch holes. Kirschbaum and Andrews⁵ obtained an efficiency of 80% for alcohol-water on plates having 0.1 inch holes. Langdon and Tobin⁶ working with 22 mm. dia. plates having 0.85 mm. holes report a maximum efficiency of 90% with CCl_4 —benzene mixture. Oldershaw⁷ using hole-sizes of 0.85, 1.1 and 1.35 mm. dia. obtained efficiencies of 102%, 84% and 72% for benzene- CCl_4 mixture.

From a summary of the work stated above it will be seen that the size of perforations, more than any other single factor, determines the efficiency of a perforated plate column. In the present work by using small hole sizes of $1/16''$ and $1/32''$ dia. very high overall efficiencies with different binary mixtures have been obtained.

One draw-back of decreasing the size of perforations is that the throughput of the column decreases. However, an economic balance may be drawn up between the throughput and size of the holes. It is definite that so

far column efficiency is concerned, sieve plate column with proper design of perforations and plate spacing will work as efficiently as a bubble cap column. The chief disadvantage of sieve plate column, however, is that the range of vapour velocity at which they can work is rather limited.

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PERFORMANCE OF SIEVE PLATE FRACTIONATING COLUMNS.
PART III. EFFECT OF PLATE SPACING AND
SUBMERGENCE

BY B. KARIM AND S. K. NANDI

CHEMICAL ENGINEERING LABORATORIES, INDIAN INSTITUTE OF SCIENCE, BANGALORE

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The effects of plate spacing and submergence on the performance of a perforated plate column have been studied with three binary mixtures : ethyl alcohol-water, methyl alcohol-water and acetone-water. It has been found that increased plate spacing gives better efficiency and also increases the capacity. With 1" submergence nearly 100% point efficiency has been obtained and further rise in efficiency has not been obtained with further increase in submergence. Overall efficiencies exceeding 100% are due to concentration gradient existing on a plate, and when reduced to point efficiency, they do not exceed 100%.

The effect of vapour velocity, feed concentration, area and size of perforations on the performance of a perforated plate column have been reported in previous parts (this *issue*, pp. 3, 12). In the present investigation the effects of plate spacing and submergence have been studied in the same $2\frac{1}{4}$ " diameter column with three binary mixtures : ethyl alcohol-water, methyl alcohol-water and acetone-water.

Effect of Plate Spacing on Efficiency

The plate spacing was varied from 6" to 12", so that in the first case number of plates used was six and in the second case, three, with a submergence of 1" in each case. Each plate had 75 holes of $1/16$ " dia. making the area of the holes equal to 5.793% of the area of the plate. Table I shows the overall efficiency and the results are plotted in Fig 1. Table II shows the individual Murphree efficiency of a particular plate with different vapour velocities for the system, methyl alcohol-water.

It will be seen that with the increase of the plate spacing from 6" to 12", remarkable increase in the efficiencies of the column in the case of methyl alcohol-water and acetone-water is obtained, while the increase in efficiency with the ethyl alcohol-water system is comparatively small. The efficiency increases from 70% to 124% in the case of methyl alcohol-water and from 33% to 111% in the case of acetone-water system, while for ethyl alcohol-water system, the increase is from 115% to 126%. This shows beyond doubt the importance of increased plate spacing in distillation columns.

The lower efficiency obtained for the systems methyl alcohol-water and acetone-water in the column having 6" plate spacing is probably due to the fact that high entrainment prevailed which drastically reduced the

TABLE I

Plate spacing.	Run No.	Reflux rate (c.c./min.)	Feed composition (mol. %).	Product composition (mol. %).	Theoretical No. of plates.	Actual No. of plates.	Overall % efficiency.
6"	Results for systems: EtOH-water, MeOH-water & acetone-water reported in Part II.						
12"	System: Ethyl alcohol—water.						
	1	20	21.15	76.46	8.78	3	126
	2	35	16.15	75.34	8.61	3	120
	3	44	10.64	72.98	8.28	3	109
	4	54	8.4	61.91	2.0	3	66
12"	System: Methyl alcohol—water.						
	5	10	20.14	90.2	2.85	3	95
	6	16	20.20	95.6	3.7	3	123
	7	28	20.20	95.7	3.73	3	124
	8	36	20.00	90.8	2.86	3	95
	9	40	20.30	90.0	2.80	3	93
	10	50	20.14	89.5	2.74	3	91
12"	System: Acetone—water.						
	11	15	7.0	92.75	3.33	3	111
	12	32	7.0	92.75	3.33	3	111
	13	36	6.8	91.1	2.83	3	94
	14	46	6.0	92.0	3.0	3	100
	15	52	5.1	82.0	1.81	3	60

TABLE II

Column having 3 plates, 75 holes of 1/16" dia., 12" plate spacing.

System: Methyl alcohol—water.

Reflux rate (c.c./min.).	Composition (mol. %)				Em ₂ %.
	V ₂ .	L ₂ .	V ₂ *.	V ₃ .	
18	89.0	84	93.2	66	66
22	90.0	65.5	85.0	59.5	119.5
28	86.0	59.25	82.0	53.2	113.5
38	76.8	41.0	73.5	46.7	108.6
44	67.4	33.5	68.0	42.0	94

efficiency of the column. With increase in plate spacing, the entrainment was negligible for the same distillation rate and the result is very remarkable. But in the case of ethyl alcohol—water, the increase is much less probably due to the fact that the loss due to entrainment for this system was comparatively low even with 6" plate spacing.

Hollbrook and Baker¹ determined the amount of entrainment for various distillation rates for plate spacings ranging from 12" to 31½". In general, doubling the vapour velocity resulted in approximately a ten-fold increase in entrainment. According to them, plate spacing is of very great importance in determining the amount of entrainment under any given conditions. A plot of log of entrainment *versus* the reciprocal of plate spacing for various vapour velocities gave straight lines. As an approximate generalisation, it was stated that cutting the plate spacing to half would result in a ten-fold increase in entrainment and a corresponding decrease in enrichment and column efficiency. R. B. Chillas in course of the discussion of the same paper, pointed out that in columns whose diameter was small in comparison with plate spacing (as is the case with the present work) much of the spray impinged on the walls which thus acted as entrainment separators. According to Souders and Brown² plate spacing appears to lose appreciable significance in permitting higher vapour velocities for spacings above 30 inches.

The effect of entrainment on column performance can be realised from the fact that starting with almost the same feed composition of the mixtures, MeOH-water and acetone-water, the enrichment obtained with a 3-plate column with 12" plate spacing is equal to, if not more than the enrichment obtained with a 6-plate column having 6" plate spacing, other conditions remaining the same.

Another great advantage of increasing the plate spacing is that the allowable vapour range is extended considerably, and hence the capacity of the column is considerably increased. This fact leads to the conclusion that larger plate spacings would give higher throughput and better efficiency, but the column cost would increase and an economic balance has to be drawn up before fixing the plate spacing.

Effect of Submergence on Overall Efficiency

The system ethyl alcohol-water was studied with 1" and 2" submergence on columns having 3 plates with 12" plate spacing, each plate having 75 holes of 1/16" diameter. The results are shown in Table III.

TABLE III

System : Ethyl alcohol-water.

Submergence.	Run No.	Reflux rate (c.c./min.).	Feed composition (mol. %).	Product composition (mol. %).	No. of theoretical plates.	No. of actual plates.	Overall % efficiency.
1"		For results please refer to Table I, runs 1-4.					
2"	1	25	12.65	75.07	3.80	3	126
	2	38	13.20	73.56	3.53	3	118
	3	48	14.16	71.80	3.00	3	100
	4	60	16.15	68.59	1.88	3	62

The efficiency appears to remain practically the same when the submergence is increased from 1" to 2". This is probably due to the fact that the efficiency recorded by 1" submergence is very high corresponding almost to 100% point efficiency and as point efficiency of more than 100% is theoretically impossible, no increase in efficiency is recorded in the case of the present work. It must be mentioned, however, that submergence does certainly affect the column efficiency, because by increasing the submergence vapour-liquid contact for a longer period is obtained resulting in an increased efficiency. If these investigations were carried out with $\frac{1}{4}$ " or $\frac{1}{2}$ " submergence, perhaps less efficiency would have been obtained.

DISCUSSION

Efficiencies above 100%.—In the present investigation overall and Murphree plate efficiencies often exceed 100% at the optimum distillation rates. This apparently paradoxical fact of efficiencies above 100% has been reported by several workers. Peavy and Baker⁸ reported efficiencies of 120% with ethyl alcohol-water mixture in bubble cap columns. Gerster, Koffolt and Withrow⁴ working with methyl alcohol-water mixture reported Murphree plate efficiencies above 100% for a series of runs, the highest efficiency obtained being 174%. Brown⁵ reported efficiency of 120% for a perforated plate commercial beer column. Brown and Souders⁶ reported Murphree plate efficiencies of 108% for commercial gasoline stabilisers. Efficiencies above or equal to 100% have also been reported by Gunness⁷, Brown and Lockhart⁸, Oldershaw⁹ and others.

It was Kirschbaum¹⁰ who first pointed out that a definite concentration gradient existed in liquid composition in plate columns because of which efficiencies more than 100% could be obtained. According to Peters¹¹ when a liquid concentration gradient existed across a plate, values of overall Murphree efficiencies greater than 100% could be obtained, because the average liquid composition would be richer than the liquid leaving the plate. Peavy and Baker¹² reported concentration gradient as high as 30% at two ends of a plate in a 18" diameter column.

In order to find out if any concentration gradient of liquid existed in the present columns under investigation, arrangements were made for taking liquid samples at two points in each plate. The effect was studied with the system ethyl alcohol-water in the column having 6 plates with 6" plate spacing, each plate containing 75 holes of $\frac{1}{16}$ " dia. One liquid sample was taken near the point where the overflow from the top entered the plate (but not from the sealing cup) and another sample was taken at a diametrically opposite point where the liquid was leaving the plate. Table IV shows the results obtained. The significance of the different symbols used in this table is as follows :

L_{2e}, L_{3e} ...Composition of liquid taken from plates 2, 3, ... near the point where the liquid is entering from top plate.

L_{21}, L_{31} ...Composition of liquid taken from plates 2, 3, ... near the point where the liquid is leaving the plate and going below

TABLE IV

System : Ethyl alcohol-water.

Column having 6 plates, 6" plate spacing, 75 holes of 1/16" dia.

	Reflux rate (c.c./min.)				
	18.	20.	27.	32.	35.
	Composition (mol %).				
L_{21}	78.00	77.28	77.89	78.47	77.26
L_{2e}	79.40	79.31	79.58	77.28	78.37
L_{31}	74.50	73.28	72.38	72.82	73.26
L_{3e}	75.00	73.50	74.92	74.15	73.20
L_{41}	68.11	65.70	65.63	67.26	65.93
L_{4e}	68.25	69.00	67.26	68.93	65.63
L_{51}	51.15	52.10	47.72	52.89	50.15
L_{5e}	53.95	54.25	49.34	53.24	50.15

It will be seen that in each plate the composition of the liquid entering the plate is slightly higher than that of the liquid leaving the plate and that a liquid concentration gradient, up to 4 mol. % in some cases, does exist. With increase in the rate of distillation the concentration gradient decreases due to violent agitation consequent on high vapour velocity. Due to existence of a concentration gradient, the average composition of the liquid in the plate is richer in the more volatile component than the liquid leaving a plate, and because of this greater concentration the vapour actually leaving a plate may be richer in the more volatile component than the vapour in equilibrium with the liquid leaving the plate. Thus, it may be possible to have overall and Murphree efficiencies above 100 %. This view is supported by Dodge¹³, Walker, Lewis and McAdams¹⁴, Sherwood and Reed¹⁵ and others.

The difference in concentration between the two successive plates and hence the concentration gradient in a plate will vary and will depend on the slope of the equilibrium curve. Due to mixing of the liquid by bubbling of vapour, the concentration gradient decreases, but the difference in concentration does exist. The effect of concentration gradient is maximum if the liquid flows in the same direction on all plates, the efficiency being slightly less in the case of the liquid flowing in alternate directions on successive plates, but the effect is minimum where the reflux is split up by arranging the downpipes in the centre and the sides on alternate plates (cf. Lewis¹⁶).

The concentration gradient of up to 4%, which has been experimentally found out to exist in the present column for the system ethyl alcohol-water, is not the maximum that is existing in a plate, but with different sampling arrangements made in the plate at the sealing cup and downpipe, it is quite

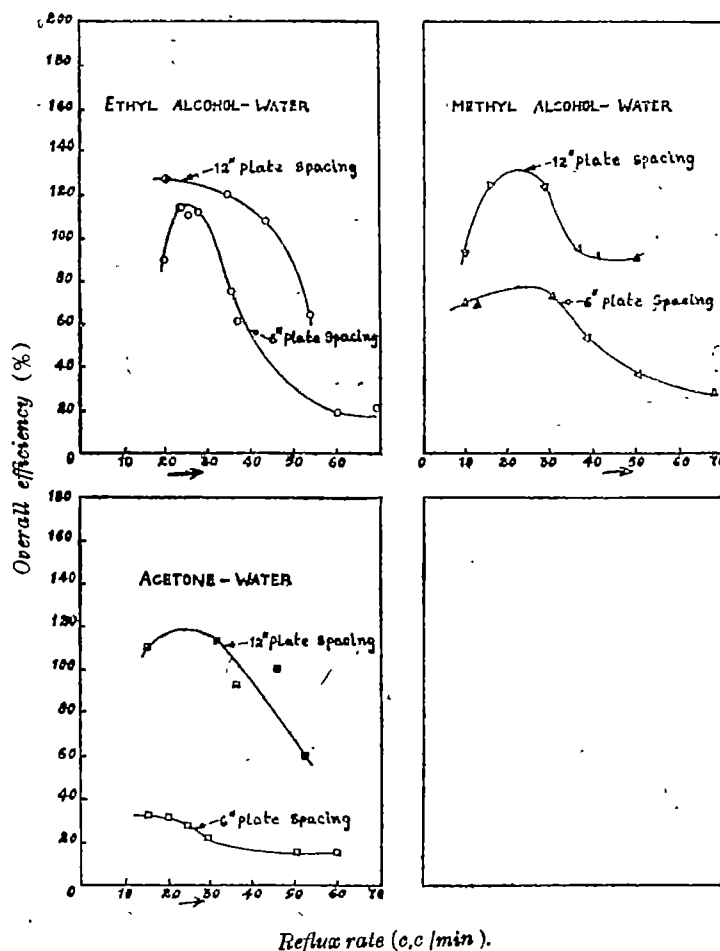


FIG. 1. Plate spacing vs efficiency.

likely that existence of higher concentration gradients could have been found out. However, assuming the existence of a 4% concentration gradient in the liquid, let us see how the Murphree plate efficiency will be affected with different ranges of concentration in the plate.

If the liquid leaving a plate is equal to 5 mol. %, the vapour in equilibrium with which is 32.5 %, the liquid on opposite end will be 9 mol. %, the vapour in equilibrium with which is 42.5 %. Assuming the vapour flow to be unmixed and if the liquid and vapour are sampled from opposite sides of the column, then

$$E_m = \frac{42.5 - 5.00}{32.5 - 5.00} = \frac{37.5}{27.5} = 130\%$$

Similarly, if the liquid leaving the plate is 10% and the liquid on opposite end is 14%, then with the same assumptions E_m is 114%; if the liquid leaving is 50%, E_m is 107%, and if the liquid leaving is 65.5%, E_m is 135%. Thus it will be seen that due to existence of the concentration gradient it is possible to have efficiencies above 100%.

Point efficiency.—Lewis¹⁶ suggested the use of point efficiency in which compositions of the vapour and liquid in a plate are taken from points lying on the same vertical plane. Theoretically point efficiencies of more than 100% are impossible, whereas the corresponding overall efficiencies may be much higher than 100%. The relation between Murphree point efficiency and Murphree plate efficiency has been mathematically deduced by Brewster¹⁷, Kirschbaum¹⁸, Hauser¹⁹, and Lewis¹⁶. According to Lewis overall efficiencies may be as high as 392%, but when reduced to local efficiency, it comes to only 100%.

With total reflux $O/V=1$, KV/O becomes equal to K , i.e., the slope of the equilibrium curve. The average slopes of the equilibrium curves for the range of concentrations involved in the different binary mixtures studied in the present work are as follows:—

	Concentration (mol. %).	Average slope (approx.).
Ethyl alcohol-water	10 to 82	0.54
Methyl alcohol-water	20 to 100	0.53
Acetone-water	5 to 95	0.4
Toluene-carbon tetrachloride	5 to 100	0.95

With the above slopes of the equilibrium curves, plate efficiencies much above 100% are possible, and it will be seen that when analysed in the light of local efficiency, the results obtained in the present work showing efficiencies above 100% are reduced to point efficiencies of less than 100%.

In the light of the foregoing it is evident that the McCabe-Thiele method of calculating performances of distillation columns does not seem to be perfect. Gerster *et al.*⁴ have proposed the H. T. U. method of Colburn and Chilton for calculating tower performances. The absurdities like efficiencies above 100% do not arise in this case. As has been proved by Withrow and co-workers⁴, this method of correlating performance data gives more systematic results than the graphical method of McCabe and Thiele²³.

Different mixtures and plate efficiency.—It will be noted that different mixtures give different efficiencies in the same columns. Gadwa²⁰ working with a column having a plate spacing of 11", width of slots 1/8" and submergence 2 to 2 1/8" obtained efficiencies of 99% for methanol-water, 83% for *n*-propanol-water, 98% for *isobutanol*-water, 90% for methanol-*isopropanol*, 75% for methanol-*isobutanol* and 82% for benzene-carbon tetrachloride. Carey²¹ using different columns reports efficiencies of different mixtures in the following order:—(1) EtOH-water, (2) benzene-toluene, (3) CCl₄-toluene. Lewis and Somley²² working with a column having 8" dia., 10 plates, 16" plate spacing and rectangular

bubble-caps having $7/8" \times 13/16"$ slots report an efficiency of 60% for benzene-toluene mixture; 75% for benzene-toluene-xylene and 80 to 95% for naphtha mixtures of pinene and aniline in naphtha.

Different efficiencies for different mixtures have been attributed to different physical properties of the mixtures, viz., relative volatility, surface tension, viscosity, latent heat, specific heat, etc. but no generalisation is possible with the data available upto now. The relative volatilities of the different binary mixtures for concentration ranges frequently involved in the present work are given below :—

System.	Conc. range	Average relative volatility.
(a) Water—ethyl alcohol	21 to 76.5%.	2.257.
(b) Water—methyl alcohol	20 to 95%.	3.647.
(c) Water—acetone	7 to 92.75%.	6.646.
(d) Toluene— CO_2	20 to 99.5%.	2.267.

The authors' best thanks are due to Sir J. C. Ghosh, Director, for his invaluable help and interest during the course of the work.

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ESTIMATION OF PENTACHLOROPHENOL IN JUTE

BY H. P. BHATTACHARJEE AND W. G. MACMILLAN

INDIAN JUTE MILLS ASSOCIATION RESEARCH INSTITUTE, CALCUTTA

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Pentachlorophenol shows a substantivity or affinity for jute. The colorimetric method for estimating pentachlorophenol (P. C. P.) on cotton, by extracting with a saturated solution of borax, acidifying the extract with hydrochloric acid, distilling, with extraction of the distilled P. C. P. in chloroform, and final treatment with a solution of copper sulphate in pyridine solution was not found satisfactory. The Catomance method, which simplifies the procedure, suggests a preliminary boil with caustic soda and subsequent distillation of the mass after acidification with formic acid gives much improved results, but the best results for jute have been obtained from a compromise between the above two methods. It depended on the preliminary boil being carried out with borax solution in place of caustic soda solution, and acidification prior to distillation with hydrochloric acid in place of formic acid. By these means it has been possible to obtain 95% extraction or recovery of P. C. P. from jute fibre.

Although the existence of P. C. P. as a chemical compound has long been recorded in the literature¹, it did not have a general commercial interest until 1936, when its properties were closely studied with regard to its use as an efficient antiseptic, highly toxic to fungi, bacteria, yeasts, algae, protozoa, and other micro-organisms. Chemically, it is pentachlorophenol. Free P. C. P. is weakly acidic and can be titrated in alcoholic solutions with caustic alkalis, using thymol blue as indicator. The sodium salts are soluble in water, while the free phenol is insoluble. As a phenol it conforms generally to the usual reactions of phenol, but the presence of five chlorine atoms renders the hydroxyl group less reactive in many instances. It distills with steam and with heavy metals forms compounds which are water-insoluble; in a number of cases these are highly coloured. The properties cited have been utilised by most of the investigators engaged in the quantitative estimation of P. C. P. It is important to observe also that care should be taken in handling the substance, since it is a skin-irritant and can cause dermatitis if allowed to remain in contact with the skin for a sufficient length of time².

A high degree of toxicity towards micro-organisms, low water-solubility, and low vapour pressure (assisting permanence), good chemical stability and availability at a relatively low price, combine to render P. C. P. particularly valuable as a preservative suitable for wood, pulp, paper, starches and dextrans, gums, proteins such as casein, albumin, gluten, leather and rubber latex, etc.³ Recently, it has been introduced in the textile industry as an anti-rot agent, and since it can be successfully applied to jute materials, a suitable method for its accurate estimation on treated jute is obviously desirable.

Deichman and Schafer⁴ estimated P. C. P. in tissues and water by spectrophotometric determination of a reddish yellow pigment formed by the action of fuming nitric acid on P. C. P., but sufficient information is not available in the literature as regards its estimation on textiles. A method for the estimation of P. C. P. on treated cotton has been described⁵ and this method depends on the extraction of P. C. P. with a saturated solution of borax, and estimating colorimetrically the P. C. P. collected, by distilling the above extract after acidification, and reacting with a solution of copper sulphate in aqueous pyridine. The method has been found satisfactory for cotton. On jute it was found that P. C. P. was incompletely extracted, only about 45% of the P. C. P. present being accounted for. Catomance Ltd.⁶ (manufacturers of the Mystox range of products containing P. C. P.) recommend a preliminary boil with caustic soda solution, collection of the P. C. P. by distillation from the whole mass after acidification with formic acid, and reacting as before. This method was found to give much improved results with a recovery approaching 90% (87.4%). The principle underlying the methods is that P. C. P. can be dissolved in a borax or caustic soda solution by a preliminary treatment of the processed materials with the above solutions. The free phenol can then be liberated on acidification of the solution and distilled quantitatively. When a chloroform extract of the distilled product is shaken with a 3% solution of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in aqueous pyridine solution, a colour develops in the chloroform layer which can be compared with that prepared similarly from a standard solution.

The object of the investigation described was to examine the above methods in more detail and determine whether these could be further improved upon.

EXPERIMENTAL

Preparation of samples.—The P. C. P. used for the experiments was obtained by distilling Dowicide VII (technical pentachlorophenol, a proprietary product of the Dow Chemical Co.) with steam and crystallising from solvent oil (b.p. $75^\circ\text{--}135^\circ$), when the product separated in fine colourless needle-shaped crystals, m. p. 184° . This refined product (0.2 g.) was weighed accurately, dissolved in chloroform and made up to 100 c. c. in a measuring flask. Requisite portions of this solution were taken and spread from a pipette over samples of jute hessian weighing 5 g. (approx.) so as to deposit known quantities of P. C. P. after evaporation of the solvent from the fabric. The samples were finally cut into small pieces and subjected to analysis.

J. T. I. Method.—The samples were transferred to a 300 c.c. Erlenmeyer flask, and treated with 100 c.c. of a saturated solution of borax. The flask was placed in a water-bath and the contents maintained at 50° for

15 minutes with frequent shaking, next filtered through a Buchner funnel and washed repeatedly with dilute borax solution. The extract (including washings) was transferred quantitatively to a 500 c.c. long-necked flask fitted with a spray trap and a vertical condenser and acidified with hydrochloric acid, diluted to 300 c.c. and distilled until 250 c.c. had passed over, the distillate being collected in a separating funnel. The distillate was shaken with three successive portions (20 c.c., 10 c.c. and 10 c.c.) of chloroform, adding from the top of the condenser so as to dissolve any adhering P. C. P. from the sides of the condenser. The combined extract was shaken thoroughly with 50 c.c. of distilled water and 2 c.c. of a 3% solution of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in a 40% aqueous solution of pyridine. The chloroform layer was run off in a 50 c.c. measuring flask and the blue aqueous layer was shaken with further small amounts of chloroform. Finally the combined extracts were made up to 50 c.c. and compared in a Hellige comparator box with a standard, prepared similarly from the 0.2% solution of P. C. P. in chloroform. The results from the experiments with cotton are shown in Table I and with jute in Table II.

TABLE I

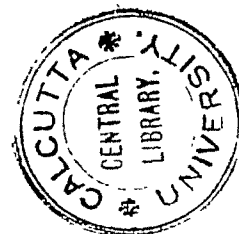
Cotton.

No. of observations.	Vol. taken.	Weight of P. C. P. taken.	found.	% of total.	% mean of total.
1	4.0 c.c.	0.008 g	0.0078 g.	91	
2	5.0	0.010	0.0096	96	
3	6.0	0.012	0.0112	93	94
4	7.0	0.014	0.0131	94	
5	8.0	0.016	0.0152	95	

TABLE II

Jute.

No. of observations.	Vol. taken	Weight of P.C.P. taken.	found.	% of total.	% mean of total.
1	4.0 c.c.	0.008 g.	0.0040 g.	50	
2	4.5	0.009	0.0043	48	
3	5.0	0.010	0.0047	47	
4	5.5	0.011	0.0049	45	
5	6.0	0.012	0.0053	44	46
6	6.5	0.013	0.0057	44	
7	7.0	0.014	0.0062	44	
8	7.5	0.015	0.0062	41	
9	8.0	0.016	0.0073	46	
10	8.5	0.017	0.0078	43	



A comparison of the above tables shows that the extraction of P. C. P. from treated jute material is very incomplete and consequently the P. C. P. retained by the jute after extraction with borax solution has been estimated. The extracted samples were taken in a 500 c. c. long-necked flask, 300 c. c. of distilled water added, followed by acidification with hydrochloric acid and the mass finally distilled. The results which are shown in Table III, account for the bulk of the unextracted P. C. P. in the first series of experiments by providing a total of some 95% accounted for.

TABLE III

No. of observations.	Wt. of P. C. P. taken.	Extract		Extracted jute		Total P. C. P. found.	Mean.
		Wt. of P. C. P. found.	% of total.	Wt. of P. C. P. found.	% of total.		
1	0.014 g.	0.0082 g.	44	0.0075 g.	54	98%	
2	0.016	0.0073	46	0.0080	50	96	95%
3	0.017	0.0073	43	0.0080	47	90	

The effect of caustic soda solution in the preliminary extraction was found by treating the samples with 20 c. c. of 4*N*-caustic soda solution and 80 c. c. of distilled water and maintaining at 50° for 15 minutes, followed by filtration through a Buchner funnel, and finally washing three times with distilled water. The extract and washings were collected, acidified with hydrochloric acid, and distilled, the results being shown in Table IV.

TABLE IV

No. of observations.	Wt. of P. C. P.		% of total.	% mean of total.
	taken.	found.		
1	0.008 g.	0.0062 g.	78	
2	0.010	0.0080	80	79
3	0.012	0.0096	80	

The substitution of the stronger alkali, caustic soda, in place of borax solution does materially improve the final result, the percentage of P. C. P. estimated being raised from 45% to 79% which percentage still remains too low for an estimation of even reasonable accuracy.

Catomanse method.—In this method the following reagents were used.

4*N*-NaOH solution, 8*N*-formic acid (368 g./lit.) in which 200 g. of ZnSO₄·7H₂O were dissolved per litre of the acid, chloroform (pure), and indicator. The indicator was made by dissolving 3 g. of pure copper sulphate (5H₂O) in

60 c. c. of distilled water and immediately before use, 4 c. c. of pure pyridine were added to 6 c. c. of the copper sulphate solution.

Preparation of standards : (1) P. C. P. (1g.) was dissolved in 100 c. c. of distilled water and 8 c. c. of *N*-NaOH and made up to 1 litre with distilled water.

(2) *N*/10-formic acid.

The requisite quantity of the P. C. P. solution was treated with 1/10th of its volume of formic acid and 250 c.c. of water in a separating funnel, extracted with chloroform, treated with the indicator solution, filtered, and made up to 50 c.c.

The treated sample was introduced into a long necked flask (1 lit.) and 250 c.c. of distilled water and 20 c.c. of 4*N*-caustic soda solution added. The mass was refluxed over a direct flame for 60 minutes, 25 c.c. of 8-*N*-formic acid-zinc sulphate solution added, and the mass distilled until some 250 c.c. had distilled over. The distillate was extracted with chloroform using 20 c.c., 10 c.c. and 10 c.c. portions, the condenser being flushed with chloroform during extraction of the distillate.

The chloroform extract was separated, treated with 2 c.c. of the indicator solution, filtered, made up to 50 c.c. and finally matched against the standards. The results, which are given in Table V, show the much increased accuracy of the method, the amount of P. C. P. found having been raised from 45% to just over 87%.

TABLE V

No. of observations.	Vol. taken.	Wt. of P. C. P.		% of total.	% mean of total.
		taken.	found.		
1	4.0 c.c.	0.0080 g.	0.0073 g.	91	
2	4.5	0.0090	0.0074	82	
3	5.0	0.0100	0.0091	91	
4	5.5	0.0110	0.0090	82	
5	6.0	0.0120	0.0111	93	87.4
6	6.5	0.0130	0.0113	87	
7	7.0	0.0140	0.0118	81	
8	7.5	0.0150	0.0137	91	
9	8.0	0.0160	0.0143	89	
10	8.5	0.0170	0.0148	87	

IJMARI method (modified Catomance method).—The test samples were first refluxed for an hour with 100 c.c. of a saturated solution of borax and 200 c.c. of distilled water, acidified with hydrochloric acid, distilled and treated in the usual manner. Table VI, in which the results are presented, shows that the yield of P. C. P. recovered from the samples under test has been still further increased, *i.e.*, from 87.4% to 95.5%.

TABLE VI.

No. of obs.	Vol. taken.	Wt. of P.C.P. taken	Wt. of P.O.P. found.	% of total.	% mean of total.
1	4.0 c.c.	0.0080 g.	0.0078 g.	97	
2	4.5	0.0090	0.0086	96	
3	5.0	0.0100	0.0098	98	
4	5.5	0.0110	0.0105	95	
5	6.0	0.0120	0.0118	94	95.5
6	6.5	0.0130	0.0125	96	
7	7.0	0.0140	0.0134	96	
8	7.5	0.0150	0.0143	95	
9	8.0	0.0160	0.0150	94	
10	8.5	0.0170	0.0160	94	

In order to determine whether the Catomance method and its modification as described could be simplified, the preliminary boils with caustic soda and borax were eliminated and the P. C. P. was distilled direct after acidification with hydrochloric acid. The procedure was to add 300 c.c. of distilled water to the sample, acidify with 1.5 c.c. of concentrated hydrochloric acid and distil direct. The results, which are given in Table VII, show that the amount of P. C. P. recovered from the sample has diminished (from 95.5% to 87.5% recovered). The pre-boil with borax solution is therefore necessary in the estimation, and most probably functions as a solvent or solubilising agent for the P. C. P. so that the latter on acidification can be distilled with a near cent per cent recovery.

In order to assess the margin of experimental error in the estimation, portions of the standard solutions of P. C. P., which were used throughout the entire series of experiments, were distilled direct after acidification in order to ascertain the possibility of complete recovery of P. C. P. Measured quantities of the solution of P. C. P. in chloroform (0.2%) were taken in a litre flask with 300 c.c. of distilled water and 1.5 c.c. of concentrated hydrochloric acid

TABLE VII

No. of observations,	Vol. taken.	Wt. of P.C.P. taken.	Wt. of P.C.P. found.	% of total.	% mean of total.
1	4.0 c.c.	0.0080 g.	0.0078 g.	91	
2	4.5	0.0090	0.0080	89	
3	5.0	0.0100	0.0092	92	
4	5.5	0.0110	0.0096	87	
5	6.0	0.0120	0.0108	90	87.5
6	6.5	0.0130	0.0112	86	
7	7.0	0.0140	0.0128	91	
8	7.5	0.0150	0.0128	85	
9	8.0	0.0160	0.0132	82	
10	8.5	0.0170	0.0140	82	

Distillation was continued until some 250 c. c. of distillate had collected and estimation of the P. C. P. in the latter was conducted in the manner already described.

The indicator solution was freshly prepared before use, since this solution can develop a slight coloration even with pure chloroform if allowed to stand for a few days. It was further found that a slight change of shade occurred in the colour of the chloroform solution obtained by the reaction of the copper sulphate/pyridine solution on standing, and this necessitated the preparation of fresh standard solutions before comparison.

The results from the series of experiments are shown in Table VIII and since the recovery of P. C. P. from the prepared solution of known concentration is of the order of 95%, which corresponds to the recovery figure from the fabric samples, the margin of 5% can be taken as the error of the method.

TABLE VIII

No. of observations.	Vol. taken.	Wt. of P.C.P. taken.	Wt. of P.C.P. found.	% of total.	% mean of total.
1	5.0 c.c. ^D	0.010 g.	0.0095 g.	95	
2	6.0 c.	0.012	0.0113	94	
3	7.0	0.014	0.0133	95	95
4	8.0	0.016	0.0153	96	
5	9.0	0.018	0.0173	96	

CONCLUSIONS

The standard method recommended for the estimation of P. C. P. on cotton was confirmed as satisfactory for this fibre, but was not found suitable for jute because only a portion of the P. C. P. could be extracted.

It appeared that P. C. P. when applied to jute was largely retained by the fibre, probably as the result of a physico-chemical union arising out of differences in the chemical composition and physical structure of the two fibres.

The Catomance method was found to give a marked improvement on the extraction of P. C. P. from treated jute materials.

An improvement on the Catomance method in which the yield of P. C. P. was increased from 87.4% to 95.5%, was obtained. The modifications consisted of submitting to a preliminary boil with borax solution instead of caustic soda, and carrying out the acidification prior to distillation with hydrochloric acid instead of formic acid.

Distillation of a solution of P. C. P. of known concentration did not increase the yield of P. C. P. found; consequently, the experimental error of the revised method could be regarded as of the order of 5%.

The use of a correcting factor (1.05) should give still more accurate results with a narrow error limit.

The authors thank the Executive Committee of the Indian Jute Mills Association Research Institute for permission to publish the results described.

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THE ROLE OF FLAVONES IN PLANT DRUGS

BY T. R. SESHADRI

ANDHRA UNIVERSITY, WALT AIR

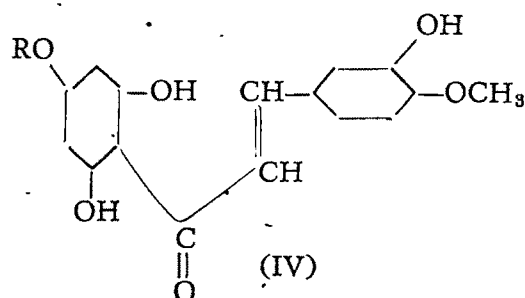
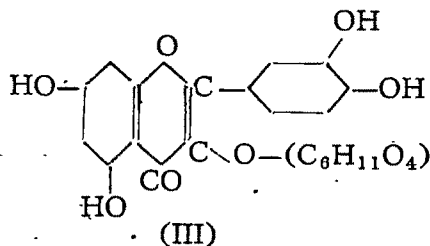
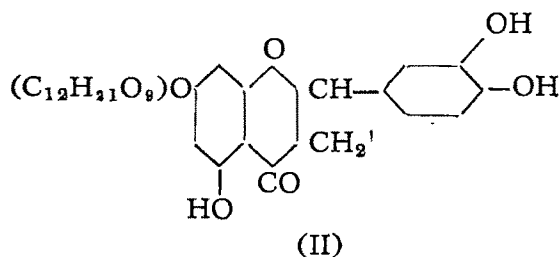
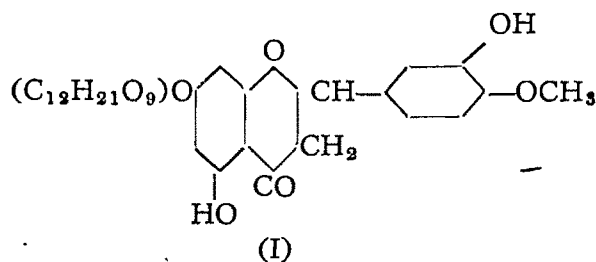
(Received February 14, 1948)

Careful chemical investigation of a number of plant drugs used in India has not revealed the presence in them of the well recognised active substances like the alkaloids and the cardiac glycosides. The only isolable crystalline components of special nature belong to the group of flavones. The tendency has been not to recognise them as the therapeutically active components, but to consider that accompanying amorphous entities of unknown nature contain the active principles. The reason is not far to seek. These compounds have been known all along as vegetable dyestuffs, now on the retreat, and few expected that they would have any marked physiological action. This attitude is not, however, correct since several synthetic dyestuffs have turned out to be drugs and the principles that govern drug action are more or less similar to those that affect dyeing properties. It has now been slowly realised that the flavone derivatives have a definite physiological action on the animal organism. Not only this, the position seems to have so developed that some of these compounds will be needed in commercial quantities again. What were once wanted only for their dyeing properties, discarded in the interim in preference to synthetic dyestuffs, are again coming into prominence as drugs.

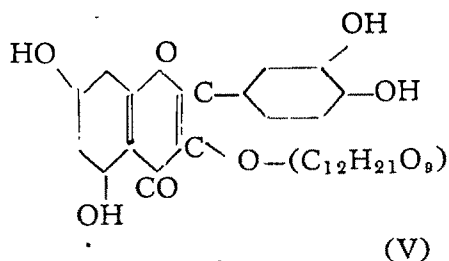
The earliest work on this subject was that of Koike¹ who investigated the diuretic action of myricetin, morin and kaempferol on normal rabbits and showed that the potency increased with increasing number of hydroxyl groups. The diuretic dose was about 25 mg./kg., the fatal dose being 8-10 g./kg. given subcutaneously. This was supported by the work of Fukuda² who showed that besides the above mentioned flavones the flavone glycosides, quercitrin, rutin and myricitrin were also diuretic. Many Chinese and Japanese vegetable drugs, known to be diuretic, were found to contain the flavone group of compounds. He further reported that they were cardiac stimulants and vasoconstrictors and that they increased blood pressure. They are absorbed in the intestinal canal and from the subcutaneous tissue and are excreted unchanged in the urine. They are also present in the bile. Fukuda further found that kaempferol and its glucoside were cathartic being the effective constituents of *semen Rhamni japonici*. Similar results were reported by other workers³. However, Sokoray and Czimmer⁴, who

studied the action of quercitrin on the blood content of abdominal organs, found that in doses of 1 mg./kg. there was a fall in blood pressure and the kidney and mesenteric vessels were affected.

But the greatest advance has been made in connection with the studies on vitamin-P. Under the term vitamin-P are included certain mixtures of flavanone and flavone glycosides which are found widely distributed in nature in many fruits. Szent-Gyorgyi noticed that there are certain symptoms of scurvy which are not cured by vitamin-C. These are associated with pathological fragility of the capillary walls and their permeability to plasma proteins and are attributed to the lack of vitamin-P. The flavanone and flavone glycosides having curative properties were first isolated from Hungarian paprika and later from lemon juice and peels, and more recently from rose hips. These are also well known rich sources of vitamin-C. The term citrin was first used for the crystalline product obtained from lemons and this was shown by Brückner⁵ to consist of a mixture of the glycosides, hesperidin (I) and eriodictin (II). Later quercitrin (III) was also found to be present. The possibility that the active principle is the glycoside of the chalcone (IV) corresponding to hesperidin (I) has also been suggested.



To the above has been added rutin (V) which is a 3-disaccharide of quercetin occurring widely in nature. The use of this substance has been considerably promoted by the United States Department of Agriculture as an adjunct in the treatment of fragile capillaries in hyper-tensive patients. As a result, it is estimated that the rutin, marketed in U. S. A. will amount to several million dollars in 1948.



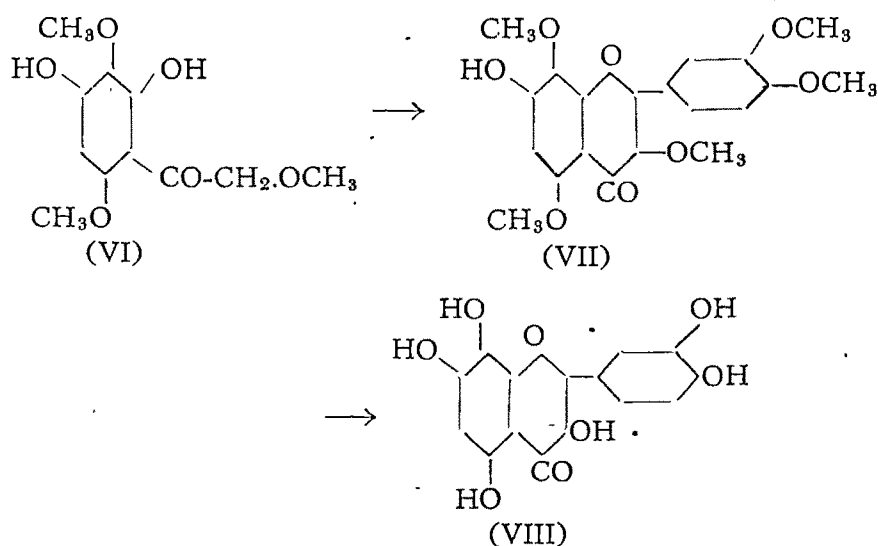
Other substances for example, aesculin, aesculetin and catechin have also been found to have vitamin-P action. According to Lavollay and Parrot⁶ their action is attributed to the protection they give to epinephrine or adrenaline, which is primarily responsible for maintaining the capillary condition satisfactory. But this theory of indirect effect does not seem to be fully accepted, the alternative of a direct action on capillary walls being also possible⁷.

In the course of such investigations it has been found that the flavanol, gossypetin (VIII), has a very powerful vitamin-P action.

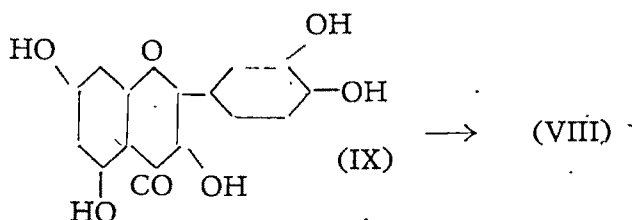
This compound was first isolated by Perkin from the Egyptian and Indian cotton flowers and studied by him to a considerable extent. Its constitution was finally established by the synthesis effected by Baker, Nodzu and Robinson⁸. Neelakantam and Seshadri⁹ had occasion to examine in detail the two important species of Indian cotton flowers, *Gossypium herbaceum* and *Gossypium indicum*. Since gossypetin is present along with herbacetin, quercetin and kaempferol, partly free and mostly in the combined form as glucosides, and since its separation is difficult, it cannot be readily and conveniently isolated from this source. Further, the yield is low. More recently however, the discovery¹⁰ that the flowers of *Hibiscus vitifolius* contain a high percentage (5%) of gossypin, a new monoglucoside of gossypetin, which is readily isolated and purified, marks an important step forward. This offers a cheap and plentiful source of gossypetin, because the plant grows wild in the Madras Presidency.

The synthetic production of gossypetin has also been rendered considerably easy as the result of recent work. The older method involved the difficult

preparation of the ketone (VI) and its condensation with veratric anhydride and sodium veratrate and subsequent demethylation,



As part of chemical studies on the biogenesis of anthoxanthins, the conversion of quercetin (IX) into gossypetin has been effected by Rao and Seshadri¹¹ by adopting the method of nuclear oxidation using alkaline persulphate:



Since quercetin is a widely occurring flavonol and is readily available from various sources, its conversion into gossypetin is economically quite feasible. One such cheap source of quercetin is the Cambodia cotton flowers¹² which fall down during the season. This cotton is very popular in South India and covers a very large acreage. The flowers as waste products can be obtained in considerable quantities.

Another interesting and recent development in this line is the discovery of the marked toxic and insecticidal properties of the simpler flavone derivatives. It started from the study of plant insecticides which led to the study of the relation between constitution and insecticidal properties. For a considerable number of years the idea has been current that insecticides owe their properties to the presence of specific groups primarily responsible for their toxicity (toxophore) and also other groups which are essential for the promotion of the insecticidal action. Lauger *et al.*¹³ have given more

concreteness to these conceptions. Among the toxophores, groups like (A) $\text{CO}-\text{CH}=\text{CH}-\text{O}-$ and (B) $-\text{O}-\text{CO}-\text{CH}=\text{CH}-$ were included and lipoid solubility was emphasised as very important for insecticidal action. These ideas can be applied to the explanation of the insecticidal action of plant insecticides like rotenone and pyrethrins as well as synthetic insecticides like D. D. T. As compounds having the grouping (A), the flavones have been tested by the present author¹⁴ using fish as test animals. It was found that chrysin (3:7-dihydroxyflavone) and galangin were considerably toxic, whereas those having more hydroxyl groups are only feebly toxic. In contrast to the hydroxy compounds, the methoxy compounds are far more toxic and this is to be attributed to improved lipoid solubility. Actually 7-methoxyflavone is found to be highly toxic and is about 1/10 as potent as rotenone. In the course of further study it has become clear that the simpler coumarins (B) and chromones (A) are not so good an insecticide as above and the presence of a side phenyl nucleus is necessary for enhanced toxicity. Thus, 3-phenyl- and 4-phenyl-umbelliferones and their methyl ethers have considerable potency. Related flavanones and chalcones are also useful as insecticides. Effects similar to those on fish have been found even with worms. The exact mechanism of this insecticidal action is not yet clear. But these experiments are mentioned here just to emphasise the fact that flavones as a group have definite physiological properties which can be used in various directions

Regarding the function of flavones in the plant organism very little is known. An easy suggestion will be that they act as light filters in view of their capacity to absorb light. That they may have more important function will be clear from the recent study of Kühn¹⁵ on crocus pollen. From this source a crystalline glycoside was obtained which even at a dilution of 1.6×10^{12} immobilised the gametes of the alga, *chlamydomonas*, while the yellow aglucone acted on the bisexual cells as a gynotermone imparting to them the property of being able to conjugate only after addition of male gametes (*i.e.* impart female characteristics to the bisexual cells). It produces this effect even in a concentration of 1 mg. in 4×10^{11} ml. The glucoside has been shown to be 3:4'-diglucoside of *isorhamnetin*. The specific gynotermone property is possessed by *isorhamnetin* and not by *quercetin* or any of the related flavones.

S U M M A R Y

In a number of plant drugs the only obtainable crystalline components of special nature belong to the group of flavones. It is necessary to recognise them as possible active principles, and physiological studies so far made are in support. The greatest advance has been made in connection with studies on vitamin-P. A number of flavone derivatives have vitamin-P properties and gossypetin is found to be the most potent. Economic methods of obtaining it

from plant sources and by synthesis are described. The simpler flavones seem to have marked insecticidal properties and are considerably toxic to fish and worms. The recent study of Kühn on the flavone glycoside of crocus pollen indicates that flavones have important functions to perform in the plant.

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COMPOSITION OF FUSEL OIL OBTAINED FROM THE DISTILLERY OF LYALL MARSHALL & CO.

BY H. G. BISWAS AND N. K. MUNSI

SIR PRAFULLA CHANDRA RESEARCH LABORATORY, BENGAL CHEMICAL &
PHARMACEUTICAL WORKS, CALCUTTA

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Due to difference in working conditions the fusel oil from one source varies greatly from that obtained from another. Dr. S. B. Dutt¹ has worked on the composition of fusel oil obtained from Kanpur and Shahjehanpur. For some time past we were isolating the main constituent of the fusel oil for our manufacturing purposes. This fusel oil was supplied by Lyall Marshall & Co. from their distillery at Darshana, now in the Eastern Pakistan. During our routine work we felt interested to know the composition of the fusel oil, particularly with a view to ascertaining the percentage of *n*-propyl alcohol, which has recently attained a great significance due to its being a principal constituent of the sweetest substance ever discovered, viz., the *n*-propoxy (1-*n*-propoxy-2-amino-4-nitrobenzene) which we tried to prepare in our laboratory; but the lack of the *n*-propyl alcohol proved a bottle-neck.

The fusel oil which was supplied to us, was a cream coloured liquid with a characteristic alcoholic smell. Its specific gravity at 32° was found to be 0.8200. It was exhaustively examined by fractional distillation and was found to consist of the following constituents: *isopropyl* alcohol, *n*-propyl alcohol, water, acetal, ethyl *isobutyrate*, *n*-butyl alcohol, *isoamyl* alcohol, *n*-amyl alcohol in combination with other higher fatty acids and their esters. The distillation was conducted in the manner shown below.

TABLE I

Total quantity taken = 2 gallons (8800 c.c.)

Fraction No.	Boiling range.	Vol.
1	80°—95°	2152 c.c.
2	95°—127°	2530
3	127°—131°	1980
3A	Residue boiling above 131°	1990
3B	Experimental loss	138
		Total 8800 c.c.

Fraction No. 1 separated into two layers on standing. The upper layer (No. 1A) was 1980 c.c. and the lower layer (No. 1B) was 202 c.c. They were individually fractionated as follows.

TABLE II

Fraction No. 1A=1980 c.c.			Fraction No. 1B=202 c.c.		
Fraction No.	Boiling range.	Vol.	Fraction No.	Boiling range.	Vol.
4	83°—90°	750 c.c.	11	83°—90°	70 c.c.
5	90°—95°	918	12	90°—95°	10
6	95°—99°	25	13	95°—99°	5
7	99°—100°	20	14	99°—100°	88
8	100°—128°	118	15	Experimental loss	29
9	128°—131°	78			
10	Experimental loss	71			
Total 1980 c.c.			Total 202 c.c.		

Fraction No. 5 separated into two layers on standing. Upper layer, Fraction No. 5A was 728 c.c. and the lower layer, No. 5B was 190 c.c. They were then individually fractionated as follows :

TABLE III

Fraction No. 5A=728 c.c.			Fraction No. 5B=190 c.c.		
Fraction No.	Boiling range.	Vol.	Fraction No.	Boiling range.	Vol.
16	83°—90°	890 c.c.	21	83°—90°	50 c.c.
17	90°—95°	182	22	90°—95°	8
18	95°—128°	80	23	95°—99°	14
19	128°—131°	114	24	99°—100°	112
20	Experimental loss	12	25	Experimental loss	6
Total 728 c.c.			Total 190 c.c.		

Fraction No. 17 separated into two layers on standing. Upper layer (Fraction No. 17A) was 103 c.c. and the lower layer. (Fraction No. 17B) was 29 c.c. The upper layer was fractionated as shown below and the lower layer was mixed with other aqueous fractions as shown later.

TABLE IV

Fraction No. 17A=103 c.c.		
Fraction No.	Boiling range.	Vol.
26	83 — 90°	65 c.c.
27	90 — 100°	2
28	100 — 128°	30
29	Experimental loss	6
Total 103 c.c.		

Fractions No. 2 and 3 were then refractionated as shown below.

TABLE V

Fraction No. 2=2530 c.c.			Fraction No. 3=1960 c.c.		
Fraction No.	Boiling range.	Vol.	Fraction No.	Boiling range.	Vol.
30	90°—95°	630 c.c.	36	100°—128°	508 c.c.
31	95°—99°	180	37	128°—131°	1130
32	99°—100°	58	38	Boiling above 131°	322
33	100°—128°	970			
34	128°—131°	690			
35	Experimental loss	2			
Total 2530 c.c.			Total 1960 c.c.		

Now, fractions boiling between the same ranges were combined together as shown below.

Fraction No.	Fractions.						Quantity (total).
39	4	11	16	21	26	(88°-90°)	1325 c. c.
40			22	12	30	(90°-95°)	648
41		6	13	23	31	(95°-99°)	221
42	7	14	24	27	17B	(99°-100°)	251
43	8	18	28	33	36	(100°-128°)	1706
44		9	19	34	37	(128°-131°)	2012

Fractions No. 41 and 42 were taken together and allowed to separate in a separating funnel.

Fractions No. 39, 40, 43 and 44 were next individually fractionated as follows.

TABLE VI

Fraction No. 39=1325 c. c.			Fraction No. 40=648 c. c.		
Fr. No.	Boiling range.	Vol.	Fr. No.	Boiling range.	Quantity.
45	83°-90°	1060 c. c.	48	83°-90°	400 c. c.
46	90°-95°	250	49	90°-95°	238
47	Expt. loss	15	50	Expt. loss	10
Total		1325 c. c.	Total		648 c. c.

TABLE VII

Fraction No. 43=1706 c. c.			Fraction No. 44=2012 c. c.		
Fr. No.	Boiling range.	Vol.	Fr. No.	Boiling range.	Vol.
51	90°-100°	178 c. c.	55	100°-128°	220 c. c.
52	100°-128°	1166	56	128°-131°	1728
53	128°-131°	232	57	Boiling above 131°	84
54	Boiling above 131°	90	Total		2012 c. c.
Total 1706 c. c.					

Again, fractions boiling between the same ranges were combined together and fractions No. 38 in Table V and Nos. 54 and 57 in Table VII were mixed with fraction No. 3A in Table I.

Fraction No.	Fractions.				Quantity.
58	45	48	(83°-90°)		1460 c. c.
59	46	49	(90°-100°)		666
60		52	(100°-128°)		1876
61		53	(128°-131°)		2010

They were then individually fractionated as shown below. Fraction No. 59 was mixed with the contents of the separating funnel.

TABLE VIII

Fraction No. 58=1460 c. c.		
Fraction No.	Boiling range.	Vol.
62	80°—83°	...
63	83°—88°	1070 c. c.
64	88°—95°	880
65	Experimental loss	10.
		Total 1460 c. c.

Fraction No. 64 was mixed with the contents of the separating funnel.

TABLE IX

Fraction No. 60 = 1876 c.c.		
Fraction No.	Boiling range.	Quantity.
66	99°—100°	34 c. c.
67	100°—105°	42
68	105°—110°	64
69	110°—114°	62
70	114°—128°	886
71	128°—131°	222
72	Boiling above 131°	66

Total 1376 c. c.

Fraction No. 66 was mixed with the contents of the separating funnel and fraction No. 72 was mixed with the higher boiling fraction.

Contents of the separating funnel separated into two layers both of which were fractionated as shown below.

TABLE X

Combined aqueous fractions = 490 c. c.		
Fraction No.	Boiling range.	Quantity.
73	83°—88°	22 c. c.
74	88°—95°	100
75	95°—99°	46
76	99°—100°	300
77	Experimental loss	22

Total 490 c. c.

TABLE XI

Combined upper layer = 900 c. c.					
Fr. No.	Boiling range.	Quantity.	Fr. No.	Boiling range.	Quantity.
78	83—88°	26 c. c.	83	110°—114°	20 c. c.
79	88°—95°	460	84	114°—128°	165
80	95°—99°	16	85	128°—131°	90
81	100°—105°	12	86	Boiling above 131°	93
82	105°—110°	18			

Total 900 c. c.

Fraction No. 86 was mixed with the fraction boiling above, and the whole solution was fractionally distilled as shown below.

TABLE XII

High boiling fraction = Total 2500 c. c.		
Fraction No.	Boiling range.	Quantity.
87	114°—128°	184 c. c.
88	128°—131°	750
89	131°—140°	1270
90	Non-volatile, deep cream coloured fraction	225
91	Loss	71

Total 2500 c. c.

Again, fractions boiling between the same ranges were brought together as shown below.

Fraction No.	Fractions.	Quantity (total).
92	63 73 78 (83°— 88°)	1118 c.c.
93	74 79 (88°— 95°)	560
94	75 80 (95°— 99°)	62
95	66 76 (99°—100°)	384
96	67 81 (100°—105°)	54
97	68 82 (105°—110°)	82
98	69 83 (110°—114°)	82
99	87 70 84 (114°—128°)	1235
100	88 71 85 (128°—131°)	3072

Fraction No. 94 separated into two layers on standing. Fractions No. 93, 99 and 89 were fractionated as shown below.

TABLE XIII

Fraction No. 93=560 c.c.

Fraction No.	Boiling range.	Quantity.
101	83°—88°	255 c.c.
102	88°—95°	255
103	Experimental loss	50
		Total 560 c.c.

Fraction No. 102 separated into two layers on standing. Fractions No. 94, 95 and 102 were mixed together and allowed to settle in a separating funnel.

TABLE XIV

Fraction No. 99=1235 c.c.

Fraction No. 89=1270 c.c.

Fraction No.	Boiling range.	Quantity.	Fraction No.	Boiling range.	Quantity.
104	105°—110°	28 c.c.	109	114°—128°	70 c.c.
105	110°—114°	54	110	128°—131°	1180
106	114°—128°	844	111	Non-volatile higher fraction	20
107	128°—131°	244			
108	Higher boiling	65			
Total 1235 c.c.			Total 1270 c.c.		

Contents of the separating funnel separated into two layers, the upper layer was 192 c. c. and the lower layer was 420 c. c. These were then individually fractionated as shown below.

TABLE XV

Upper layer=192 c. c.			Lower layer=420 c. c.		
Fraction No.	Boiling range.	Vol.	Fraction No.	Boiling range.	Vol.
112	90°- 95°	100 c. c.	116	90°- 95°	199 c. c.
113	95°- 99°	8	117	95°- 99°	23
114	100°-128°	74	118	99°- 100°	184
115	Experimental loss	10	119	Experimental loss	14
Total 192 c. c.			Total 420 c. c.		

Fractions boiling between the same ranges were brought together as shown below.

TABLE XVII

Boiling range.	Quantity.	Composition	Correct B. p.	Percentage in fusel oil.
88-88°	1373 c. c.	<i>iso</i> . Propyl alcohol	84°	15.602
88-95°	299 c. c.	mixed <i>iso</i> . propyl and <i>N</i> -propyl alcohol	...	3.867
95-99°	31 c. c.	<i>n</i> -Propyl alcohol	97°	0.852
99-100°	618	Water	100°	7.022
100-105°	54	Acetal	104°	0.618
105-110°	110	<i>iso</i> Butyl alcohol	108°	1.250
110-114°	136	Ethyl <i>isobutyrate</i>	110°	1.545
114-125°	938	<i>n</i> -Butyl alcohol	116°	11.227
128-131°	4496	<i>iso</i> Amyl alcohol	129°	51.090
Non-volatile fraction	245	2.784
Loss	450	5.113

To facilitate a comparative study the results of Dr. Dutt on his work on the fusel oil from Messrs. Begg Sutherland & Co. Ltd., Kanpur are furnished below :

Ethyl alcohol	...	0.057%	Acetal	...	0.124%
<i>iso</i> Propyl alcohol	...	2.230	<i>iso</i> Butyl alcohol	...	0.227
Mixed <i>isopropyl</i> &			Ethyl <i>isobutyrate</i>	...	0.165
<i>n</i> -Propyl alcohol	...	0.018	<i>n</i> -Butyl alcohol	...	0.968
<i>n</i> -propyl alcohol	...	0.237	<i>iso</i> Amyl alcohol	...	85.230
Water	...	5.150			

From a comparison we find that our sample is much richer in *isopropyl* alcohol and much poorer in *iso*amyl alcohol than Dr. Dutt's sample and unluckily both the samples are too poor in the much sought for *n*-propyl alcohol.

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VOLATILISATION OF PHOSPHORUS AS HALIDES (A PRELIMINARY NOTE)

BY PHANINDRA NATH MUKHERJEE AND H. N. DAS-GUPTA

DEPARTMENT OF APPLIED CHEMISTRY, UNIVERSITY COLLEGE OF
SCIENCE & TECHNOLOGY, CALCUTTA

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During recent years pyrolytic methods of producing phosphorus, phosphoric acid or compounds of phosphorus have been receiving a great deal of consideration¹. Even some of the quantitative methods are based on evolving phosphorus from phosphates in suitable forms by the application of heat. Thus, Jannasch and Heimann² had evolved a quantitative method of volatilising phosphorus from ammonium or magnesium phosphate. The process, in short, consists in subjecting a mixture of the phosphate, canesugar syrup and sulphuric acid to the action of chlorine, followed by oxygen at an elevated temperature. This was simplified by replacing the current of chlorine with carbon tetrachloride vapour and dispensing with the use of carbonised sugar³. Subsequently, further improvements were made and phosphorus in phosphates of Fe, Cr, U, Zn, Ni, Co or Mn was successfully estimated. These metals are retained in the experimental combustion tube as chlorides, whilst the phosphorus, probably in the form of phosphoryl chloride, is collected in a receiver, containing dilute nitric acid. The success of the reaction, however, depends on the maintenance of a bright red heat temperature.

From an analysis of the reaction, involved in the above process, it can be inferred that at first phosphorus pentachloride is perhaps formed by the interaction of chlorine and elemental phosphorus. The phosphoryl chloride is subsequently produced by the decomposition of phosphorus pentachloride by small traces of associated moisture. This may also be produced by the interaction of unchanged phosphorus pentoxide and phosphorus pentachloride as :



The production of phosphorus pentachloride can be accounted for from the findings of Jacob and Reynolds⁴. They have shown that calcium phosphate has certain definite dissociation pressure at temperatures varying between 1050° and 1200°, and at these temperatures free phosphorus pentoxide is reduced very rapidly by carbon. This, naturally, causes corresponding increase in the rate of dissociation of calcium phosphate. Thus, elemental phosphorus becomes gradually available for transformation into halogen derivative. On the basis of the above facts, it was considered useful to realise the feasibility of isolating

phosphorus primarily as a halide, by passing a current of dry chlorine or dry hydrogen chloride gas over an anhydrous mixture of calcium phosphate, carbon and silica at a comparatively low temperature. Silica was used purposely, as it tended to accelerate the dissociation of tri-calcium phosphate⁵.

Results of preliminary experiments go to show that it is quite possible to prepare halides of phosphorus at temperatures in the vicinity of 950°, provided access of moisture is rigorously excluded. Difficulty, however, was experienced in condensing the volatilised products, even with elaborate condensing systems. But this difficulty can be overcome by installing a Cottrell precipitator in the system. From qualitative analysis it was found that the evolved product was a mixture of phosphorus trichloride, phosphorus pentachloride and phosphoryl chloride. The % conversion, so far obtained, is not high, as this depends on a number of factors. Further work, with a view to obtaining a satisfactory yield of phosphorus pentachloride is in progress.

EXPERIMENTAL

The raw materials consisted of bone ash (P_2O_5 , 32.8%), charcoal (fixed carbon, 80%) and quartz powder (SiO_2 , 99%). Each was separately ground to pass through 80 mesh sieve. An intimate mixture of the ingredients (contained in a silica boat and the quantity shown in respective tables) was first dried at 120° and then introduced in a silica combustion tube (1 meter in length and 1.5 cm. dia.) placed in an electric furnace. One end of this tube was connected to a source of dry chlorine or dry hydrogen chloride gas. The other end of the tube was connected to a system of four empty receivers, each of which was provided with a condenser. These receivers were connected in series. To prevent access of moisture the exit end of the last receiver was provided with a calcium chloride guard tube. The entire system was freed from air by maintaining a constant flow of dry chlorine or dry hydrogen chloride gas. For each experiment the temperature of the furnace was raised to 950° and maintained at that for 2 hours. With the onset of the reaction, the entire apparatus was filled with dense cloudy fumes, a small fraction of which could be condensed in the receiving system as a slightly pasty mass. If, however, the fumes were bubbled through water, acidulated with nitric acid, cent per cent absorption took place. For estimating the percentage of P_2O_5 evolved, this latter procedure was adopted. The slightly pasty fraction, condensed in the receiver, was yellowish white in colour, and on analysis it was found to be a mixture of chlorides of phosphorus and phosphoryl chloride.

In addition to time and temperature, the rate of volatilisation depends on the proportions of carbon and silica. The extent to which volatilisation of

phosphorus takes place, from a mixture of bone ash and varying proportions of carbon, has been shown in Table I. The same weight of each mixture was separately exposed to the influence of chlorine and hydrogen chloride gas. In each case the operation was conducted for 2 hours at 950°.

TABLE I

Calcium phosphate.	Carbon.	% P_2O_5 volatilised using HCl gas. Chlorine.	
7.14 g.	2.9 g.	10.1	12.3
6.6	3.4	12.3	16.1
5.0	5.0	14.1	16.6
3.4	6.6	14.5	16.8

Table II embodies the experimental results obtained with silica. The rate of volatilisation of P_2O_5 was found to increase with increased concentration of silica.

TABLE II

Heated for 2 hours at 950°.

Batch No.	Bone ash.	Carbon.	Quartz.	% P_2O_5 volatilised using HCl gas. Chlorine.	
1	5.0 g.	5.0 g.	0.0 g.	14.3	16.5
2	4.5	4.5	0.87	22.1	24.3
3	4.4	4.4	1.3	29.2	32.1
4	4.2	4.2	1.6	36.0	39.1
5	3.9	3.9	2.3	45.1	47.2
6	3.6	3.6	2.8	46.5	52.1

In order to study the effect of time on the progress of reaction, experiments were repeated under identical conditions with batch No. 6 and the results, so far obtained, are shown below.

TABLE III

Gas used : chlorine		Gas used : Hydrogen chloride.	
Duration.	P_2O_5 volatilised.	Duration.	P_2O_5 volatilised.
1 hr.	29.3%	1 hr.	28.7%
2	51.8	2	47.9
3	59.1	3	51.8

From the above table it is to be noted that hydrogen chloride gas is almost equally efficient in producing halides of phosphorus.

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DETERMINATION OF SELENIUM AND TELLURIUM IN REFINED COPPER

By K. P. GHOSH

CHEMICAL LABORATORY, METALLURGICAL INSPECTORATE, TATANAGAR

(Received March 11, 1948)

Selenium and tellurium are usually found associated with copper ores so the refined copper frequently contains small amounts of these two metals.

Methods for the determination of the two elements in refined copper, as given in some of the books, are found not to be very satisfactory, due presumably to the minuteness of the quantity in which they are present in copper. In some cases, no trace even of Se and Te could be found on account of the long and round-about process, they prescribe.

Sulphur dioxide is the most usual precipitant for selenium and tellurium, and they can be obtained directly by passing SO_2 in the nitric acid solution of copper, but not free from it, while hydroxylamine hydrochloride may more conveniently be used for the precipitation of both the metals.

Se and Te can be precipitated from the nitric acid solution as dioxides, when the refined copper is dissolved in nitric acid and with iron, and the iron is precipitated as hydroxide with ammonia whereby most of the copper, silver, nickel, etc. are eliminated. Again Se and Te can be precipitated from a hydrochloric acid solution of the iron hydroxide by a 20% solution of stannous chloride. Now the metals are free from Bi, Sb and As but may occlude a little tin and copper.

If these metallic precipitates, in turn, are dissolved in strong hydrochloric acid, saturated with bromine, boiled and a solution of hydroxylamine hydrochloride added, Se and Te, will come out as metals free from other impurities.

These precipitates can be easily washed with hot water and alcohol, while precipitates obtained by SO_2 are apt to pass through the asbestos mat of the Gooch crucible on washing with hot water.

Process.—The sample (10g.) was dissolved in 50 c. c. of strong nitric acid, iron drillings (0.5 g.) added, the solution diluted to 300 c. c. and boiled till all the iron drillings were completely dissolved.

The solution was cooled and treated with an excess of ammonia to precipitate ferric hydroxide along with Se and Te as dioxides. The precipitates were then filtered in a big funnel on a 15 c.m. paper and washed with hot ammoniacal

water, and dissolved in hot hydrochloric acid (1 : 2) in a conical flask, the filter being washed with the same acid. The solution of the iron precipitate in hydrochloric acid was boiled, stirred and treated with a freshly prepared 20% solution of stannous chloride (dropwise). The solution first became colourless and on continued addition turned reddish brown or brown or brownish black in colour after which it was allowed to settle for 3 to 4 hours. The black precipitate contained the whole of the Se and Te, and the separation from Bi, Sb and As was complete, as the acid concentration was not high enough to precipitate arsenic. There might be some copper and tin, contaminating the precipitates.

The precipitate was filtered on pulp and washed with hot water. The water in the stem of the funnel was drawn out, and the precipitate was dissolved and washed carefully with 15 c. c. of concentrated hydrochloric acid, saturated with bromine, into a small beaker. The solution was diluted to 30 c.c. and 10% solution of hydroxylamine hydrochloride (10 to 15 c. c.) was added to it and boiled and allowed to settle overnight. Se and Te precipitated out as metals free from all other impurities. These were filtered in a burnt and weighed Gooch crucible, washed with hot water, alcohol and dried for 2 hours at a temperature of 105° and weighed. The difference between the two weights gave the weight of the metals in 10g sample.

TABLE I

(1) Sample of 36th batch of refined copper, sampled on 20-5-43 at Ghatsila.	
0.1 g. of SeO_2 added.	Without addition of SeO_2
Wt. of Se and Te ... 0.0728 g.	Se and Te ... 0.0012 g.
added Se ... 0.0712 g.	... 0.0012%
Se and Te ... 0.0014 g.	Reported 0.013%
i. e. 0.014%	
(2) Sample of refined blister copper, 2nd portion, 2nd voyage, sampled on 26-6-43 at Ghatsila.	
0.1 g of SeO_2 was added.	Without addition of SeO_2 .
Wt. of Se and Te ... 0.0728 g.	
added Se ... 0.0712 g.	Wt. of Se and Te ... 0.0012 g.
0.0016 g. = 0.016%	... 0.012%
	Reported 0.014%
(3) Sample of blister copper, 35th batch, 3rd portion, sampled on 5-4-43.	
Wt. of Se & Te = 0.0014 g.	
= 0.014%	

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NOTES & NEWS

Anti-static Surface for Plastics

Many plastics pick up and hold a static electric charge on their surfaces. In addition to the disadvantageous electrical properties, the surface attracts lint and dust which is very difficult to remove due to the strong electrical attraction. This was overcome in the past, at least on a temporary basis, by rubbing the surfaces with various so-called anti-static agents.

The use of a special synthetic wax by incorporating it in the molding gives excellent anti-static properties to the surfaces and gives good anti-blocking action at the same time. As a specific example, 1% or less Acrawax C powder is incorporated into a vinyl copolymer molded product. Product A, containing Acrawax C, and Control B, without Acrawax C, were rubbed with a cloth which left lint on the surface. The lint remained stubbornly on B even when subjected to a strong blast of air and rubbed with a lintless material. The lint was easily removed from A by a simple blow of air from the mouth or could easily be dusted off with a lintless material or by a small air blower.

Based on this discovery, many types of plastics that ordinarily pick up harmful static charges or become obscured and dirty by lint, dust, etc., can now be made free from these hazards. The Acrawax C powder, which is manufactured on a large scale by the Glyco Products Co., Inc., at

their plants in Brooklyn, N. Y. and Natrium, W. Va., can be used successfully on plastic sheeting and packaging films and on parts that are rubbed, touched or moving rapidly (as on shafts).
H. B.

Instruments Designed by the A. C. S. I. R.

Many ingenious and scientific devices and instruments have recently been developed by the various Divisions of the Australian Council for Scientific & Industrial Research. In connection with plant and horticultural investigations, an electrical apparatus is at present being used for physiological work. It effectively measures the electrical resistance of plants, and can be used to indicate whether tissue is dead or only weakly unresponsive, and shows also its moisture content. It is claimed to be more sensitive than moisture metres, frequently used for phases of this work, and is only half as expensive.

For the measurement of the movement of water in soil formations, the Soils Division is using two instruments known as the Ring infiltrometer and the Spray infiltrometer. They are used for comparative work. The wetted soil around a small test plot of the spray infiltrometer has indicated that it restricts lateral movement sufficiently to make results comparable with those which would result if a large area were watered by spray irrigation.

The Soils Division has also developed a new type of soil thermometer. It enables temperature to be measured indirectly from the electrical resistance of a solution of sodium chloride in a small cylinder located near the gypsum block. It uses a simpler measuring apparatus than the one frequently used with thermocouples, and in the field it can be used for measuring the resistance of both gypsum blocks and standard thermometers.

Another Division investigates frost by means of a sounding balloon which records conditions at levels up to 400 feet. The suitability of a selected district for horticulture is closely linked with its relative "frostiness". This Division of the Council also exposes thermometers in various positions over the selected area and compares the readings with those obtained in districts already producing crops.

In the field of metrology the Council's officers designed and manufactured a special type of hydrometer for measuring the density of milk. This followed a request received from the Milk Board of the State of New South Wales, which stated that there were certain apparent discrepancies between the weight of milk loaded into railway tank cars at a country depot, and the weight received at the city depot.

The hydrometer satisfactorily determined the correct weights, and it can be used with equal accuracy for both clear and opaque liquids.

For the general measurement of mass and associated quantities, Australia is at present employing the most up-to-date equipment. A reference standard

kilogram and a reference standard pound have been received on loan from the National Physical Laboratory, London, and the Council will shortly possess the largest equi-arm balance in Australia. It will be used for the calibration of large capacity measures up to 10 gallons.

Because of the growing demands by expanding industry in Australia for advice and assistance in Vibration measurement, an electromagnet vibration pick-up was designed and constructed locally. The pick-up connects to a cathode ray oscilloscope which indicates the magnitude and wave form of the vibration to be measured. The apparatus has found considerable practical use, mainly in the balancing of rotating machinery, such as steam turbines. A miniature design is being developed, and will weigh only four ounces.

Australian electro-technologists are now busy on a design for a differential analyser, which will differ from the conventional type of instrument in that electrical interconnection will be used between the various units. It will be used in investigations concerning radio propagation. It is claimed that the interconnection system in this type of mathematical machine considerably reduces the setting-up time for a given equation.

For research work in physics, a new optical pyrometer has been made for the measurement of high temperatures. In the conventional optical pyrometer the filament does not appear of uniform brightness, and consequently cannot be made to disappear completely against the background of the hot body

upon which the operator desires to sight the instrument. The Australian researchers have found that the obscuring of the filament may be considerably improved by including a suitably oriented polarising screen in the eye-piece. This also permits of larger apertures, and results in desirable accuracies.

R. C.

C. B. C. C.

The objective of the Chemical-Biological Co-ordination Centre of the National Research Council is to test and record the biological activity of thousands of chemical compounds so that the information on these compounds may be available for scientists seeking better drugs, insecticides and chemical agents essential to agriculture and medicine. Such records will surely help in the early realisation of the usefulness of newly discovered chemical compounds and will minimise the chance of many chemicals and drugs losing their usefulness under gathering dusts in the laboratory.

Another important function of the centre is to compile technical "records on the effects of chemical structures upon various kinds of biological activities and on the test methods used in the study of such activity". (*Chem. Eng. News*, March, 1948).

B. K. M.

Synthetic Production of Radio-active Isotopes

Investigators on radio-active elements predicted as early as 1923, that there should be four independent disintegra-

tion series rather than the three natural radio-active series then known. As a result of investigations extending over a period of 6 to 7 years, Prof. Glenor T. Seaborg, Director of Chemistry in the Radiation Laboratories, University of California, has synthetically produced an entire series of radio-active isotopes which will form "a fourth new radio-active family". It is pointed out that one of the important isotopes in the series U^{238} is fissionable with neutron and thus there is every possibility of its becoming a "nuclear fuel". The key member of the series (Np^{237}) is an isotope of a transuranium element (neptunium), and, in addition, two other transuranium elements (plutonium and americium) are represented in the direct line of decay.

B. K. M.

Vinyon N

This new chemical fibre consisting of a vinyl chloride-acrylonitrile copolymer has been recently introduced to the American public. The Carbide and Carbon Chemicals Corporation has built a 1,300,000 \$ production unit for this fibre. The resin is made from a mixture of about 40% acrylonitrile and 60% vinyl chloride and is claimed to produce yarns superior to vinyl chloride-acetate fibres. The finished yarn can be dyed, spun and woven and has all the qualities of vinyl resins so far as resistance to chemical, mildew and fungus attack is concerned.

The resin is doped with acetone and a stabiliser in nitrogen atmosphere. A solution with 20% solids content is obtained which is then filtered, the temperature being maintained between

75° and 90° and finally spinned. The spun yarn has relatively little strength and to obtain the desired strength, the yarns are plied ends together and stretched. The stretched yarn is finally subjected to a heat modification treatment which imparts tenacity, high yield point and low ultimate elongation. (*Chem. Eng. News*, March, 1948).

B. K. M.

Ethylene Glycol

Ethylene glycol was a laboratory curiosity a few decades ago. It now plays an important role in many manufacturing and industrial operations. In 1944, there was maximum demand for glycol; six million gallons were used then for war purposes, for the manufacture of explosives, for anti-freeze purposes in combat planes and used in the radiators of cars operating in the African desert to prevent undue vaporisation of water.

The Dorr Chemical Co. of Canada, Ltd. have since January 1948, started a glycol plant with an output of 3 million gallons, the anticipated requirements for several products such as shampoo, candy, chewing gum, solvent, lubricant, plasticiser, heat transfer medium, etc., besides its chief use as a freezing point depressant. (*Canadian Chemists & Industries*, March, 1948).

B. K. M.

Radio-active Materials Stimulate Plant Growth

The results of experiments conducted at Toronto on some selected agricultural products such as carrots

cabbages, tomatoes, beans and potatoes, indicate that that radio-active materials, when used in combination with commercial fertilisers, increase the yield. It is suggested that the radio-active elements activate the chemicals in the fertiliser.

B. K. M.

A Vital Point to Chemical Industry

Many will be surprised to hear the statement "the chemical industry is the heaviest consumer of capital" made at a symposium on Commercial Chemical Development, held in New York where the directors of chemical industries discussed their problems in connection with development and sale.

It was stated that 1.4 billion dollars were spent in 1947 for new plants and equipments for the chemical industry.

B. K. M.

New Advances in Fermentation Industries

Fungal amylase, which is produced in thin stillage by *Aspergillus niger*, is reported to produce alcohol from grain more economically than the present standard methods.

Another new development is the production of riboflavin by aerobic fermentation using *Ashbya gossypii*. (*Chem. Eng. News*, March, 1948).

B. K. M.

New Solvent Ethers for Grignard Reagents

It has been found that relatively non-volatile ethers, such as dibutyl

ether, diphenyl ether, anisole, diethyl carbinol can well replace inflammable ethyl ether in Grignard reaction. The usual Grignard catalysts, such as iodine and magnesium iodide, were found to be effective in promoting the reaction in other solvents. Temperatures of reactions in the presence of catalysts were lower than those without them.

This observation is expected to be of some industrial importance in the manufacture of silicones and other processes (organo-metallic compounds) where Grignard reaction is essential. (*Chem. Eng. News*, March, 1948).

B. K. M.

Mysore Silk vs Japanese Silk

The economic price of silk produced in Mysore is Rs. 32/8/- per lb. The Government of India have, however, recently imported Japanese silk at Rs. 18/- per lb. f. o. b. Japan. The sale price of this silk in Indian Union will come to Rs. 27/12/- per lb when protective duty at 25%, specific duty, surcharges, and probable expenses are taken into consideration. It is therefore apparent that the indigenous industry will be handicapped unless the present rate of import duty is enhanced. Silk produced in India played an important part during the last war in the manufacture of parachutes and it is hoped that silk industry in India should be afforded a protective tariff.

B K. M.

The Use of Aluminium in Food Industry

The use of aluminium and its alloys in Food Industry was the subject of

scientific survey at the Low Temperature Research Station at Cambridge. It has been made known that foodstuffs can be cooked in aluminium vessel without destruction of vitamins and other food values. It has also been proved by experiments upon rats that there is no possibility of producing any organic disease or food poisoning by the use of aluminium vessels. The feeding experiments on rats showed that the metal was completely excreted and "the growth and fertility in the rats were completely normal even to the fifth generation." Aluminium and its alloys are being extensively employed in dairy industry for fabrication of mechanical milking, pasturising and churning machines. Although fruit juices in cold do not corrode the metal, hot juices of certain fruits do react, which of course, is prevented to a large extent in presence of sugar.

B. K. M.

Pulping Qualities of Bamboo Chips

An investigation on the pulping qualities of crushed and uncrushed bamboo chips has shown that the thoroughly crushed chips yield on digestion with alkali highest percentage of both bleached and unbleached pulps. These pulps are more uniform in quality, and require the least percentage of standard bleaching powder for the production of a good white shade. (*Indian Forest Bull.*, No. 127). R. C.

Ammonium Nitrate as Fertiliser

Prior to 1942, this chemical was used as a fertiliser compounded with limestone or ammonium sulphate

(Nitro-chalk, Cal-nitro, Lennasalpeter). A company in California has recently placed on the market 83% aqueous solution of ammonium nitrate for direct use in irrigation work. It has now been demonstrated that nearly pure solid ammonium nitrate can be used for direct application to crops. It gives good results under a wide range of crop, soil and climatic conditions.

Ammonium nitrate is one of the cheaper sources of nitrogen for the soil. A unit of nitrogen (20 lbs.) costs the farmer about the same amount in ammonium nitrate as in the form of ammonium sulphate and less than in the form of nitrate of soda. It supplies to the soil not only ammonia-nitrogen but nitrate-nitrogen also. (*Chem. Eng. News*, April, 1948).

B. K. M.

Electronic Mechanism in Analytical Chemistry

The modern trend towards instrumental analysis from physical properties was discussed in a symposium on "Modern methods of analysis" at the University of Minnesota.

Dr. James Hillier of R. C. A. reports that as a result of his study on the mechanism of reproduction of viruses by electron microscope, strong evidences have been adduced that the theory of chemical synthesis of viruses is closer to the truth than the oldest hypotheses of reproduction by division after the manner of living cells.

Ludo K. Frevel of the Dow Chemical Co. divulged for the first time the technique that had been developed to utilise X-ray absorption for the elemental analysis of organic compounds. The first automatic apparatus designed for the process has been described.

Peter Debye of the Cornell University reviewed the method for the determination of molecular weight from excess humidity as a result of light scattering in solutions.

Supersonic Waves Harnessed in Industry

The industrial utilisation of supersonic waves has now become an accomplished fact. Different characteristics of sound waves provide the basis for its utilisation in diverse fields. The physical impulses of sound waves are utilised in liquid emulsification and aerosol agglomeration. The characteristic that sound wave travels at different speeds in different media is utilised in identifying and distinguishing individual materials. (*Chem. Eng. News*, March, 1948).

B. K. M.

Minerals in Madras Presidency

Salem district in Madras is rich in deposits of iron, bauxite and magnesite ores. The iron ores have been found to be practically free from P and S, and are very suitable for the manufacture of high quality wrought iron or steel. According to the survey report of the Geological Dept. the iron ore reserve is estimated to be 904,650,000 tons and it is expected that in actual working 3 or 4 times this quantity may be available. The Shevaroy hills in this district are rich in bauxite and the reserves are estimated to be about 4,275,700 tons. Limestone and dolomite are also available in the Salem, Trichinopoly and Coimbatore districts. Fireclay, magnesite, chromite and quartzites deposits also occur within short distances

of the iron ore deposits. In South Arcot, not too distant from Salem, a reserve of about 498 million tons of lignite (average c. v. 9000 B. T. U.) have been proved to exist. B. K. M.

Victoria Jubilee Technical Institute, Bombay and the College of Engineering and Technology, Jadavpur, as interim relief to be adjusted against grants for future years.

Grants for Technical Institutions

The following capital grants for buildings and equipment and interest free loans repayable in 33 years for construction of hostels have been sanctioned by the Central Govt. for the year 1947-48 subject to certain conditions which are intended to ensure the proper utilisation of the grants :—

Institutions.	Capital grant.	Interest free loan.
Victoria Jubilee Technical Institute, Bombay.	2,00,000	80,000
College of Engineering & Technology, Jadavpur, Bengal	2,00,000	2,80,000
Benares Hindu University, College of Engineering	80,000	80,000
College of Mining & Metallurgy	30,000	60,000
University of Calcutta—Dept. of Applied Chemistry, Dept. of Applied Physics	2,25,000	50,000
Andhra University—Jaipur Vikram Deo College of Science & Technology	70,000	...
Madras University—Alagappa Chettiar College of Technology	60,000	...
Nagpur University—Luxminarayan Institute of Technology	1,10,000	28,000

Additional amounts of Rs. 2,00,000 each have been sanctioned for the

Acharya Prafulla Chandra Memorial

The collections for the Sir P. C. Ray fund have been augmented by the kind donation of the entire collection of the Sir P. C. Ray 80th Birthday Celebration Committee and the total sum so far collected amounts to Rs. 42,589/-

An Advisory Committee consisting of Sir J. C. Ghosh and Prof. M. N. Saha representing the Birthday Celebration Committee and Sir S. S. Bhatnagar and Dr. B. C. Guha (latter two elected by the Council of the Indian Chemical Society) has been formed to give effect to the proposals for perpetuating the memory of the savant in an appropriate manner.

The Committee elected Prof. N. R. Dhar to deliver the first Memorial Lecture on August 2, 1948 in the University College of Science, Calcutta where the revered scientist used to live and breathed his last.

On the same day the unveiling of the oil painting of the late Acharyadev will be performed.

Silver Jubilee Celebration of the Indian Chemical Society

The Indian Chemical Society has completed the 25th year of its existence on 6th May, 1948. The Council has decided to celebrate the silver jubilee of the Society during the Science Congress

week at Allahabad in January, 1949, so that the largest number of Fellows from all over India may participate in the function. The function, as provisionally fixed, consists of (i) publication and presentation of a souvenir brochure together with a jubilee badge, (ii) a special jubilee celebration meeting, (iii) the election of Honorary

Fellows, (iv) a number of symposia and (v) Silver Jubilee lunch, followed by the Annual General Meeting, (vi) popular lectures.

A Silver Jubilee Fund has been opened to receive voluntary contributions from the Fellows and sympathisers of the Society to meet the expenses for the purpose.

The cost of publication of this issue has been partly borne out of the generous contribution made by the Rockefeller Foundation, received through the courtesy of the National Institute of Sciences of India.

REVIEWS

Fundamentals in Chemical Process Calculation—By OTTO L. KOWALKE. PUBLISHED BY MACMILLAN COMPANY, NEW YORK. 168 Pages. Price 14 Sh.

The book is meant for students of Chemical Engineering. Fundamental laws of physics and chemistry are, stated, followed by problems related to chemical industries and process operations. Data given in these problems are not imaginary or arbitrary but are drawn from actual practice. It is a good book for the students of Chemical Engineering and Applied Chemistry. In Indian Colleges and Universities in the teaching of Chemistry, not much stress is laid on the applied side, at least not in a quantitative manner. Data in the problems set for the students are always in grammes and cubic centimeters. Students should be taught to think of these figures in industrial quantities and relations. The book will be very helpful for teachers of general chemistry also to select problems and illustrations.

H. L. R.

Linseed Oil and its Products—By S. D. VIDYARTHI. PUBLISHED BY JAIDEVA BROS., BARODA. Pp. 58+50. Price Rs 8/-

This is a booklet dealing with refining and utilisation of linseed oil. The author thinks that this will help the manufacturers. Although for a high standard work and actual technology the publication will have no value at all, it may perhaps help a student

for preliminary study, if properly edited. It contains numerous misstatements *e.g.* (a) Chapter II, in p. 20, the break is assumed to be 10%, whereas in actual practice it hardly exceeds 0.2% by wt. (b) Chapter V, p.3 - the percentages of metal in metallic soaps are not correctly recorded. (c) Chapter VI, p.16—the raw oil is bleached by the minimum quantity of driers of which cobalt resinate is very efficient—this is entirely wrong.

The author is advised to revise the book before formal presentation to the public.

M. G.

Methods of Vitamin Assay—PREPARED & EDITED BY THE ASSOCIATION OF VITAMIN CHEMISTS. INC. PUBLISHED IN 1947 BY INTER-SCIENCE PUBLISHERS INC., NEW YORK. Pp. 189+XVII. Price \$ 3.50.

The interesting book 'Methods of Vitamin Assay' comes at an opportune moment when we are busily engaged in planning to put our drugs and medicaments on a perfect footing. The Drugs Rules are being implemented and the Pharmacy Act is being enforced. Vitamins, which are now-a-days largely used by the public and the medical practitioners, would have to be standardised as to their quality and potency. As such to those who would be engaged in test examination and analyses of vitamins and vitaminised products, this book will prove invaluable not only by providing information of the standard methods of vitamin assay,

but also by offering relevant literatures that may help in further improvement of the methods of standardisations and analyses of these important products

The main part of the book deals with the assay of vitamin A, carotene, thiamin, riboflavin, niacin and ascorbic acid. A chapter has been added with numerous references on the methods of estimation of vitamin D, E & K, and biotin, folic acid, *p*-amino-benzoic acid, inositol, choline, pantothenic acid and pyridoxine. The last chapter is on check samples in the control of vitamin methods. It must be said that the publication is not a comprehensive treatise on vitamin assays but a simple and handy manual for the analysts. Details starting from the preparation of the sample to be assayed up to the final calculation, have been presented in an elegant style. The whole treatise is a merited attempt to make the procedures intelligible

even to "a laboratory technician with limited training in quantitative analysis".

The book deals mainly with the methods that have been successfully applied to a variety of goods or other materials; but as now-a-days pure vitamins are also largely used in medicine and medicinal products, it would be welcome if chemical methods for some of the vitamins, wherever possible, be included in a subsequent edition of the manual

The printing is excellent and the sequence of chapters proves much care in editing for which the authorities of the Association of Vitamin Chemists deserve congratulation. The book will be a valuable addition to libraries interested in vitamin chemistry and would be indispensable for those engaged in the analysis and assay of vitamins.

U. P. B

CHANGE IN VISCOSITY AND DEGREE OF RIPENESS OF VISCOSE CAUSED BY ADDITION OF REAGENTS

BY L. THORIA

TECHNOLOGICAL LABORATORY, INDIAN CENTRAL COTTON COMMITTEE, BOMBAY

(Received June 23, 1948)

Degradation of the micelle is the only known means of lowering the viscosity of a solution of cellulose or of its compound. Scherer and Leonards, however, reported that small additions of certain reagents lowered the viscosity of viscose solutions without affecting the micellar dimensions. In view of the great industrial advantages that could accrue from such a development, the effect on the viscose solution of 18 different reagents was studied. Of these only 8 viz., pyridine, sodium sulphite and sodium nitrite succeeded in lowering the viscosity of the viscose, others having either no appreciable effect or an adverse one. The lowering of viscosity appeared to be a function of the amount of chemicals added. No attempt was however made to explore optimum condition, as it was found in the meanwhile that the viscose solution, whose viscosity was lowered in this manner, did not become ripe in the normally allotted time and had to be ripened longer, during which time the viscosity went on rising. The ultimate result was that what was gained by the lowering of the viscosity, was virtually lost by the reduction in the ripening speed, except for a negligible resultant advantage of 2-3% lowering in viscosity under optimum conditions.

The work, conducted under the auspices of the Indian Central Cotton Committee, envisaged the use of chemical cotton as a base for manufacturing rayon by the viscose process. Chemical cotton, particularly when it is purified with care, possesses a much higher viscosity than the ordinary rayon pulp. It is an established fact that rayon, produced from a high viscosity viscose, is stronger than that produced from a low viscosity one, but the high viscosity of viscose presents technical difficulties, particularly with regard to filtration and spinning, which have yet to be surmounted. Thus, although the yarn qualities make the use of high viscosity viscose desirable, the limitations of our present day technique of manufacturing rayon do not permit it. Under the circumstances it appeared as though there was no alternative but to degrade chemical cotton intentionally, in order just to make it fit for viscose manufacture.

At this juncture, a very interesting article by Scherer and Leonards¹ on "Change in viscosity of viscose by addition of reagents" appeared. This apparently was the very first attempt to lower the viscosity of the viscose through a selective adsorption by the xanthate particle of the reagent, which would then form part of a colloidal particle aggregate, less lyophilic than the original xanthate particle, without causing any damage to the structure of cellulose. The only reagent, which was found by the authors to thus reduce viscosity, was pyridine. The idea, however, was fascinating and was followed up in the hope of avoiding the need of degrading the high grade cellulose in order to make it technically fit for rayon manufacture. Unfortunately however, the hope has been frustrated to a very great extent by the findings reported in this paper, as the degree of ripeness was overlooked by the American workers.

E X P E R I M E N T A L

Procedure.—A sample of cut chemical cotton was mercerised in 18% caustic soda solution for 2 hours at 18° with 1:15 bath ratio. The mercerised cellulose was then pressed to three times its dry weight and shredded in a specially constructed disintegrator for 1 hour, to give it the desired fluffiness. These alkali cellulose flakes were then allowed to ripen for 4 days at 18° in a closed bottle.

The ripened alkali cellulose was then xanthated in large glass bottles, which were rotated during the entire period of reaction, keeping the reaction conditions uniform for all the series of xanthations reported in this paper.

The cellulose xanthate, thus obtained, was then dissolved in 3% caustic soda solution, 10 times the weight of dry cellulose. The resulting viscose was each time subdivided into 4 different bottles. To three of these bottles were added measured quantities of the reagents under test, whereas to the fourth was added an equal quantity of distilled water to ensure for a uniform concentration in each bottle. The viscosity, as also the degree of ripening, were then measured as shown in the tables and the change brought about in these characteristics by the reagents calculated on the basis of the viscose containing no reagent.

The viscosity of the viscose was measured by the falling sphere method and the degree of ripeness by addition, of a 10% ammonium chloride solution. As the actual values for viscosity in terms of seconds of the original (to which no reagent is added) xanthate solutions of the various series were not uniform, it appeared more useful and instructive to record the changes not in actual time measured but in the percentage rise or fall in viscosity brought about by the reagent as compared with the original one. Gelling time has also been recorded in case of the first two tables

The quantity of the reagent added to the viscose has been expressed in terms of percentage on the weight of viscose. Wherever solutions are used, the percentage is expressed in terms of the active reagent itself, excluding water.

Table I below shows the effect on the viscosity of viscose, caused by 16 different reagents, organic as well as inorganic. The first 5 of these have caused a reduction in viscosity and extended the gelling period. The following 3, namely, Nos 6-8 have practically no effect on viscosity, but they too extend the gelling period appreciably. The next two, *i.e.* No 9 and 10 influence neither the viscosity nor the gelling period. No. 11 registers a small fall in viscosity followed by a small rise but without any effect on the gelling period. The last five reagents, represented by Nos. 12-16, show a definite rise in viscosity accompanied by a shortening of the gelling period except in case of No. 12, which has no effect on the latter property.

TABLE I

Change in viscosity of viscose by addition of reagents

No.	Chemical added.	% Addition on wt. of viscose.	% Lowering in viscosity after		Extension or shortening of gelling period** by number of days.
			5 days.	8 days	
1.	Pyridine	0.53	2	...	1 day more
2.	Na ₂ SO ₃	0.083	2	...	2 " "
3.	NaNO ₂	0.014	4	8	2 " "
4.	*Tetrachloroethylene	0.4	5	...	1 " "
5.	Acridine in pyridine (sat.)	1.4	3	10	2 " " 1 " "
6.	*Toluol	0.4	Negligible		
7.	Urea	0.038	"		2 " "
8.	KH ₂ PO ₄	0.083	"		2 " "
9.	*CCl ₄	0.4	"		No change
10.	cycloHexanone	0.4	"		Do
11.	Acetonitrile	1.0	1 (rise in viscosity)		Do
12.	Amyl acetate	0.4	6	7	Do
13.	40% Formaldehyde	0.16	34	...	4 days less
14.	Chloroform	0.4	26	48	2 " "
15.	Ethylene chloride	0.4	87	...	4 " "
16.	Dichlorhydrine (1:2)	1.25	8 " "

* These chemicals are not miscible with viscose.

** The gelling period in case of the viscose to which no reagents were added was generally found to be 11 days.

Table II reproduces the effect of the quantity of the reagent on the reduction in viscosity of viscose in case of the first 3 numbers of Table I, tetrachloroethylene having been discarded as it is not miscible with viscose, and acridine, because the solvent used is pyridine which itself is being tested.

TABLE II

Quantitative effect of certain reagents on the change in viscosity of viscose

No.	% Addition on wt. of viscose.	% Lowering in viscosity after		Extension or shortening of gelling period.	No.	% Addition on wt. of viscose.	% Lowering in viscosity after		Extension or shortening of gelling period.	No.	% Addition on wt. of viscose.	% Lowering in viscosity after		Extension or shortening of gelling period.
		5 days	8 days				5 days	8 days				5 days	8 days	
A. Pyridine. B. Sodium sulphite. C. Sodium nitrite.														
1	0.53	2	—	1 day more	0.033	2	—	2 days more		0.014	4	8	2 days more	
2	0.66	2	8	„ „	0.084	4	10	„ „		0.23	5	10	„ „	
3	1.33	3	10	2 days „	0.42	9	16	3 „		—				

The obvious conclusion from the data presented in Table II would be to carry on these tests with increasing quantities of the reagents concerned as long as the reduction of viscosity continues. But, since the degree of ripening is an important factor in spinning, and in view of the fact that the viscose under normal spinning conditions should have a degree of ripening, as determined by 10% ammonium chloride solution, of the magnitude of 8-10, it was decided at this stage to observe the effect on the degree of ripening of viscose caused by the addition of these three reagents which affect the viscosity favourably. Table III reproduces the change in degree of ripening of viscose brought about by these chemicals added in varying quantities.

TABLE III

Change in the degree of ripening of viscose caused by the addition of varying quantities of certain reagents

% Addition on wt. of viscose.	Degree of ripening after			% Addition on wt. of viscose.	Degree of ripening after			% Addition on wt. of viscose.	Degree of ripening after		
	4 days	5 days	6 days		4 days	5 days	6 days		4 days	5 days	6 days
1. Sodium sulphite.				2. Sodium nitrite.				3. Pyridine			
Nil	16.0	8.0	5.4	Nil	10.0	6.0		Nil	10.0	6.5	
0.42	27.0	15.5	8.0	0.83	9.0	6.0		0.06	13.0	8.5	
0.81	27.0	15.5	8.5	0.46	9.5	6.0		1.32	13.0	8.5	
1.22	27.0	15.5	8.0	0.69	8.5	5.5		1.98	10.5	7.0	

It is clear from Table III that the degree of ripening does not remain unchanged, the magnitude of the change from the original viscose depending upon the type of reagent, as also upon the amount of the same reagent

added to the viscose. In view of this fact it was thought proper to measure both the viscosity as well as the degree of ripening on the same viscose before drawing any conclusion from data so far obtained. The variations observed in these two properties, as a result of the addition of pyridine and sodium nitrite in different quantities, are reproduced in Table IV. Sodium sulphite was discarded from these experiments as it is clear from Table III that it slows down the process of ripening to such an extent that no advantage could be expected from the reduction in viscosity caused by that reagent. Each number denotes a separate series, in which the same viscose is used for tests.

TABLE IV

*Change in viscosity and degree of ripening of viscose
caused by addition of reagent*

No.	Chemical added.	% Addition on wt. of viscose.	4 Days after xanthation		5 Days after xanthation	
			% Lowering in viscosity.	Degree of ripening.	% Lowering in viscosity.	Degree of ripening.
A.						
1	Nil	—	—	15.5	—	9.0
	Pyridine	0.5	2	20.0	4	12.0
	Sodium nitrite	0.086	3	15.5	3	9.5
2	Nil	—	—	18.0	—	10.5
	Pyridine	1.0	4	22.0	4	12.5
	Sodium nitrite	0.17	3	18.5	3	10.0
3	Nil	—	—	11.5	—	8.5
	Pyridine	2.0	3	18.5	4	9.5
	Sodium nitrite	0.34	2	14.0	1	8.0
4	Nil	—	—	18.0	—	8.0
	Pyridine	3.0	3	18.0	1	12.0
	Sodium nitrite	0.52	Negligible	12.0	1% Rise	7.5
5	Nil	—	—	15.0	—	9.0
	Pyridine	4.0	3	21.0	7	14.0
	Sodium nitrite	0.69	Negligible	15.5	1% Rise	9.0
B.						
1	Nil	—	—	7.5	—	5.5
	Pyridine	2.0	3	9.0	3	6.0
	Sodium nitrite	0.17	3	7.5	5	5.5

DISCUSSION

Scherer and Leonards¹ have shown that the addition of pyridine to viscose reduces its viscosity. They have also shown that the reduction in the viscosity of viscose is directly proportional to the quantity of the reagent added, of course, up to a certain limit. This observation has been substantiated by the present work. It has further been found that not only an organic substance like pyridine with its unwelcome odour and with its narrow limit of miscibility, but harmless inorganic substances like sodium sulphite and sodium nitrite, which can be added in any quantity to the viscose, also bring about the desired reduction in the viscosity, as can be seen from Table I.

Moreover, it can safely be deduced from Table I that those chemicals, which reduce the viscosity of viscose, necessarily extend the gelling period, while those which increase the viscosity contribute to the shortening of the gelling period. What is, however, likely to prove valuable to the industry is the observation that certain chemicals, such as urea, bring about an extension of the gelling period although they have practically no influence on viscosity. This point needs close study from the industrial point of view, not only because the extension of the gelling period is a desirable feature, but also because of the possibility of the yarns made from such viscose exhibiting special properties.

Table II represents a quantitative study of the effect of addition of pyridine, sodium sulphite and sodium nitrite on the viscosity of viscose. Whereas pyridine and sodium nitrite bring about approximately the same reduction in viscosity, within the range of experiments, sodium sulphite causes considerably greater reduction in the viscosity than the other two. If reduction in viscosity were the only criterion to evaluate these reagents, sodium sulphite would decidedly be preferable to pyridine, as the same reduction in viscosity can be achieved by a much smaller quantity of the former than of the latter, which can moreover be added to any extent.

But does a mere reduction in the viscosity of viscose by itself mean an advantage from the technical point of view? It is well known that the spinning of rayon is not regulated by the viscosity of the viscose alone. The degree of ripening is a factor which cannot be neglected, as it is in all probability of even greater importance than viscosity in view of the fact that it determines the coagulation velocity of the viscose during the process of spinning. The reduction in viscosity, to be real, must therefore be obtainable to the maximum extent at a point when the viscose has attained the degree of ripening essential for spinning, say about 8-10. According to Scherer and Leonards¹, addition of 5% pyridine brings about a reduction of 30% in the viscosity of viscose after 316 hours. But this gain is certainly not real, as the degree of ripening does not remain unaffected by the presence of the reagent in the viscose.

Table III reproduces the effect of the three reagents under consideration on the process of ripening. Each of them behaves differently. Sodium sulphite very considerably reduces the speed of ripening, thereby showing clearly that what is gained by way of reduction in viscosity is lost by way of reduction in the speed of ripening, the net gain being that the viscose can be spun a day or two later. It deserves to be noted that the effect on the degree of ripening is independent of the quantity of sodium sulphite added to the viscose, whereas the effect on viscosity is a function of the quantity added. Sodium nitrite has practically no effect on the speed of ripening, while pyridine retards the speed of ripening up to an addition of 2%, at which concentration the speed of ripening remains more or less unaffected. The effect of still higher concentrations of pyridine on the degree of ripening of viscose will be seen from Table IV, which also gives the change in viscosity.

Let us first observe the effect of pyridine on viscosity and speed of ripening of viscose, as depicted by Table IV (A). After a lapse of 5 days, when the blank attains the degree of ripeness necessary for spinning, the viscose containing varying quantities of pyridine is found to be definitely lagging behind in ripeness. Only in case of 2% pyridine, the degree of ripeness is more or less the same as that exhibited by the blank, but on either side, *i.e.* at lower as well as at higher concentration of pyridine, there is a distinct fall in the speed of ripening of viscose. Turning to the effect on viscosity, it will be observed that at this ripening period only 4% reduction in viscosity is achieved except in the case of 4% pyridine, which shows a higher reduction *i.e.* 7% in viscosity, but a degree of ripeness, not sufficiently advanced for spinning. If, however, this viscose is allowed time to attain the required degree of ripeness, the gain in the form of reduction of viscosity would vanish, as the viscosity, which is a function of time, would not stand stationary but go on increasing until gelling takes place. It follows therefore that only that reduction in viscosity, which is obtainable at the technically essential ripeness of viscose, denotes the real gain. The optimum concentration for pyridine therefore is 2% and the reduction in viscosity of viscose brought about by that quantity of pyridine is 4%.

Sodium nitrite has no effect on the speed of ripening, as the degree of ripening, attained by viscose containing varying quantities of this reagent, shows the same degree of ripening as the blank. This being the case, the optimum concentration of sodium nitrite would be what gives the maximum reduction in the viscosity of viscose. It will be seen from Table IV (A) that the maximum reduction in viscosity is attained at 0.17% concentration and its magnitude is only 3%, of course at the time when the viscose is ripe for spinning. A further rise in concentration of the reagent has a reverse effect on viscosity and has therefore to be avoided. The optimum concentration for sodium

nitrite is therefore 0.17% and the reduction brought about in the viscosity of viscose at that concentration is only 3%.

In a fresh series, reproduced in Table IV (B), both these reagents, viz. pyridine and sodium nitrite were added in optimum concentration to the same viscose and their effect on the viscosity and degree of ripening observed under identical conditions, when the viscose had attained the technically required degree of ripening. The net gain is the same in both cases, viz. 3% reduction in viscosity of viscose. Apparently this is not an attractive finding for the industry.

S U M M A R Y

The change in viscosity of viscose brought about by the addition of 16 different reagents was observed. Only the following three were found to reduce the viscosity :—

(a) Pyridine, (b) sodium sulphite and (c) sodium nitrite. The reduction in viscosity was found to be a function of the ripening period as also of the quantity added. The maximum reduction in viscosity was found to lie near 8% in case of pyridine and near 0.23% in that of sodium nitrite. The maximum was not ascertained in case of sodium sulphite, which definitely reduced viscosity to a much greater extent than the other two reagents.

But in view of the fact that the reduction in viscosity does not by itself denote any gain unless it is obtainable at a stage when the viscose is ripe for spinning, the determination of the degree of ripening was brought into the scope of this investigation and the effect on the speed of ripening of viscose due to the addition of pyridine, sodium sulphite and sodium nitrite, was ascertained. Pyridine at 2% concentration had practically no effect on the speed of ripening but at either higher or lower concentrations it did retard the speed of ripening appreciably; sodium sulphite effected a very considerable retardation of the speed of ripening, irrespective of concentration; whereas sodium nitrite had no effect on the ripening of viscose at all.

Both the degree of ripening as well as the viscosity were determined on the same viscose to which varying quantities of pyridine and sodium nitrite were added. It was found that at a stage, when the viscose reached the ripeness required for spinning, the maximum reduction in viscosity, and this was only 3%, was obtained by either 2% pyridine or 0.17% sodium nitrite. In all other cases the reduction in viscosity was smaller or the viscose not ripe enough for spinning.

The magnitude of the reduction in viscosity is apparently too small to attract the attention of the industry, unless a more effective reagent is found out.

R E F E R E N C E

1. Scherer & Leonands, *Rayon Textile Monthly*, 1942, Oct. No.

RECOVERY OF ELEMENTARY SULPHUR FROM FUEL GASES

BY SUDHIR SEN AND H. N. DAS GUPTA

DEPARTMENT OF APPLIED CHEMISTRY, UNIVERSITY COLLEGE OF SCIENCE &

TECHNOLOGY, CALCUTTA

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A dry process for recovery of elemental sulphur from fuel gases is described. The advantage claimed for the process is that there is no necessity of an extraction step to recover the S. The established findings regarding the reaction between H_2S and oxides of nitrogen are criticised. It is claimed that (i) the reaction products depend on conditions of reaction and at ordinary temperature NH_3 and H_2O are formed; (ii) the presence of moisture does not adversely affect the progress of reaction, and (iii) the deposited S does not retard the forward reaction. The efficiency of the reaction is enhanced when packed towers are used. It is further observed that the precipitation of elemental S is better with N_2O_3 than with NO_2 .

The recovery of sulphur, as a bye-product from manufactured fuel gas, is at present a common practice in Europe. Just before the second World war, Germany probably exceeded all other European countries in her capacity to increase the tonnage of sulphur production from fuel gas. According to Powell¹, the bye-product sulphur, recovered from coke-oven gas alone, amounted to 10,000 metric tons in 1927. This figure slowly increased to 13,000 metric tons in 1932, and then rapidly increased to 32,000 metric tons in 1937; and the estimated figure for 1938 was about 50,000 metric tons. During the last 25 years the U. S. A. also had made tremendous progress in this direction, and, as a result, the recovery of sulphur from fuel gas is at present a rapidly growing industry there. In India, however, no attempt has yet been made to recover sulphur from coke-oven or manufactured fuel gas. According to Chowdhury and Dutta² (Recovery of elementary sulphur from gases containing H_2S), about 10,000 tons of recoverable sulphur are lost annually in the various coke-ovens in India. The total amount of coal, raised annually in Bengal and Bihar, is about 19 million tons³. This is utilised as follows:

Coke-oven plants	...	5 million tons (approx.)
Stack burning for soft coke manufacture	...	1.5 " " "
Industries	...	5 " " "
Railways	...	7 " " "
Gas works	...	0.5 " " "

In accordance with Chowdhury and Dutta², it is quite reasonable to expect the feasibility of recovering approximately 30,000 tons of sulphur from about 14 million tons of coal, which amount is utilised for purposes other than industries. In this connection it may be of interest to point out that the total quantity of sulphur (both elemental and combined), imported

through the port of Calcutta alone, is of the order of 42,000 tons. This figure has been partly estimated and partly derived from the latest available Government statistics. This may not be strictly accurate, it may be regarded as conservative, erring on the low rather than on the high side.

Commercial processes, aiming at recovery of elemental sulphur from manufactured fuel gas, are many and varied, but, they have been broadly classified into wet and dry processes. It is rather difficult to judge precisely the efficiency of one class over the other. Thus, all recovery of sulphur from fuel gas in the U. S. A. is secured by the so-called liquid purification processes. Again, in Germany, there had been great activity along the liquid purification processes during the pre-war days, yet, only 25% of the recovered sulphur were obtained by the adoption of these methods. The remaining 75% of the recovered sulphur came from the well known iron oxide dry purification process (Powell²). In dry processes, however, there is an extraction step, usually involving the use of CS₂ as the solvent for the elemental sulphur⁴.

In the present communication it is proposed to describe a dry process for the precipitation of elemental sulphur from H₂S, accompanying manufactured fuel gas. In this process there is no need for the installation of a solvent extraction step. The process, in short, consists in contacting the gaseous mixture with oxides of nitrogen in a system of packed towers at atmospheric temperature. Under this condition the sulphur is deposited on the surface of the packing materials. The deposited sulphur is ordinarily of plastic type, but it can be loosened of its grip if a stream of water be passed over the packing materials. This appears to be a distinct advantage over the iron oxide process, as no solvent is necessary for removing the deposited sulphur. The oxides of nitrogen, suitable for precipitating sulphur of sulphuretted hydrogen, are nitric oxide and nitrogen peroxide. Experiments have shown that the reaction between nitrogen peroxide and hydrogen sulphide is more rapid and more readily visible than that between NO and H₂S. Most satisfactory result is obtained when a mixture of NO and NO₂, in proportions to form N₂O₃, is allowed to react.

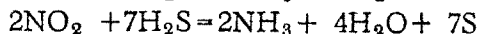
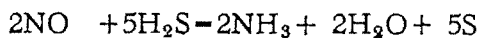
It appears from literature that experimental data, involving reactions between H₂S and oxides of nitrogen, are very meagre. Thomson and Laconte⁵ studied quite independently the reaction between NO and H₂S, but they put forward discordant views. Thomson claimed that NO and H₂S must react, yielding ammonium sulphide and a small trace of nitrous oxide. The counter-claim of LaConte is that these gases do not react at all. Pierce⁶, while not agreeing with the findings of the previous workers, made a detailed study of the reaction. His conclusions, in a summarised form, are as follows.

(1) The reaction between NO and H₂S must proceed under all conditions to yield sulphur, nitrogen and water, as, $2\text{NO} + 2\text{H}_2\text{S} \rightarrow 2\text{S} + \text{N}_2 + 2\text{H}_2\text{O}$.

(ii) The rate of reaction increases with increased surface in the reaction chamber. The reaction is also accelerated in presence of a catalyst like chemically pure silica gel, either alone, or impregnated with ferric oxide.

(iii) The deposited sulphur exhibits an inhibitory effect on the progress of the reaction and perfectly dry gases do not react.

From our findings, however, we could not corroborate fully the observations of any of the previous workers. Firstly, the nature of the resultant products depends on the conditions under which the reaction is allowed to take place. Thus, at atmospheric temperature and in the presence of packing materials, the reaction products are sulphur, ammonia and water. It is highly probable that the reactions take place as follows :



If, however, the gases are allowed to react at an elevated temperature, preferably in presence of a catalyst, they yield a mixture of sulphide and polysulphides of ammonia. Secondly, the dry gases do react spontaneously but it is very difficult to maintain a dry condition, as one of the products of reaction is moisture. Thirdly, moisture exerts no deleterious effect on the progress of the reaction, but, on the other hand its presence has a distinct advantage. Fourthly, the deposited sulphur does not retard the forward reaction.

It may be pointed out that a portion of the oxides of nitrogen, required for this reaction, may be produced from ammonia, obtained in the process.

EXPERIMENTAL

The apparatus, for studying the interaction of dry H_2S and NO , consists of three graduated aspirator bottles (capacity, each 3 litres), connected in series by glass tubes, fitted with stop-cocks. Each bottle is provided with a separating funnel at the top, and one outlet T-tube at the bottom. A sketch of the apparatus is shown in Fig 1. The two extreme bottles A and C are used as reservoirs for H_2S and NO respectively, while, in the central bottle B, the reaction is allowed to take place. The resultant gaseous mixture in B is taken out for analysis *via* the outlet tube D.

The sulphuretted hydrogen was prepared from reagent quality antimony sulphide and acid, and the nitric oxide from ferrous sulphate, potassium nitrate and sulphuric acid.

At the outset, the entire apparatus was freed from moisture by passing hot dry air for sometime. Each bottle was next completely filled with white oil, dried over metallic sodium. The end bottles A and C were filled respectively with pure and dry H_2S and NO . Definite volumes of the two

gases were sucked in the central bottle B. There was immediate reaction between them as was indicated (i) by contraction in volume, (ii) by the deposition of a coating of free sulphur on the walls of the reaction vessel, and (iii) by a rise in temperature. The pressure inside the reaction vessel was made atmospheric, and the final volume of the residual gases was noted. Each experiment was repeated twice. In the first, the residual gas

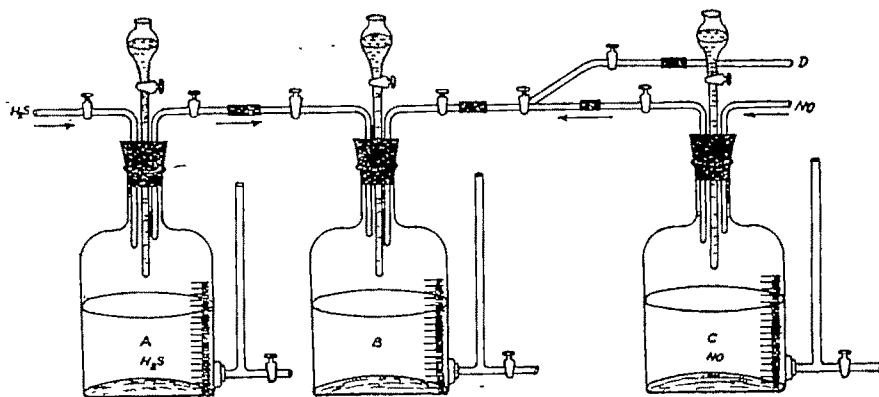


FIG. 1

mixture was analysed immediately after the reactants were mixed. In the second experiment the reactants were allowed to remain in the reaction vessel for full one hour before the analysis was made. From qualitative analyses, the residual gas in each case was found to contain a mixture of ammonia, water vapour, and unreacted H_2S and NO . The deposited sulphur, on analysis, was found to contain a minute trace of ammonium sulphide. Only, the proportions of H_2S and NO were determined quantitatively by the standard methods, and the values thus obtained were converted into volumes. The progress of the reaction will be clear from Table I.

TABLE I

Vol. of reaction mix.		Duration of reaction	Final vol.	Proportions by vol. of H_2S and NO in the residual gas.
H_2S .	NO .			$\text{H}_2\text{S} : \text{NO}$
705 c.c.	275 c.c.	5 min.	225 c.c.	18.5 : 0.2
705	275	60	220	17.5 : 0.11
460	150	5	150	82.0 : 0.6
460	150	60	100	52.0 : Trace
305	100	5	100	55.0 : 0.15
305	100	60	90	54.3 : 0.1

It may be pointed out here that exact measurement of the volume of the residual gaseous mixture was not possible, as the oil exerted its solvent action on them. From the above table it is clear that dry gases too do initiate the reaction. Similar experiments were repeated with NO_2 and a mixture of NO and NO_2 and in each case the result was the same.

Recovery of Sulphur from Coal Gas

In order to study this, artificial mixtures of the following compositions by volume were made: Coal gas, 97 to 99%; H_2S , 1 to 3%

The apparatus consisted of two graduated aspirator bottles of different dimensions. The bigger one (capacity, 10 litres). was used as a reservoir for coal gas containing H_2S , and the smaller one (capacity, 5 litres) for NO . These bottles were connected in parallel, *via* two manometers, to a system of two towers of equal dimensions and joined in series. The diameter and height of each tower were 3" and 24" respectively. The outlet from the second tower was connected to a third aspirator bottle (capacity, 10 litres), where the resultant gaseous mixture was collected for analysis by displacement of white oil.

Gases from the two reservoirs were simultaneously forced in at the bottom of the first reaction tower. The velocity of the reacting gases was maintained constant prior to their entry into the tower, but, the volume ratio of H_2S to NO was kept, as far as practicable, at 5:2. This was found feasible by using connecting tubes of different diameters and by adjusting the screw clips. The deposition of sulphur took place mostly in the reaction towers (about 98% of the total deposited sulphur) and only a small fraction of it in the last aspirator bottle for collecting the resultant gaseous mixture. The resultant gaseous mixture was analysed according to standard methods, at different intervals, to find out the proportion of H_2S still left. From Table II an idea, as to the extent to which it is possible to remove H_2S from coal gas, will be obtained. In all these experiments unpacked towers were used.

TABLE II

Vel. in ft/min. of each gas prior to its entry into the reaction tower.	Interval after which the ana- lysis was made.	S deposited (% of the total).	Vel. in ft/min. of each gas prior to its entry into the reaction tower.	Interval after which the ana- lysis was made.	S deposited (% of the total).	Vel. in ft/min. of each gas prior to its entry into the reaction tower.	Interval after which the ana- lysis was made.	S deposited (% of the total).
Vol. % of H_2S in coal gas = 1.			Vol. % of H_2S in coal gas = 1.4.			Vol. % of H_2S in coal gas = 3.0		
0.2	Immediately	73.4	0.4	Immediately	76.4	0.4	Immediately	86.0
0.3	"	74.2	0.4	1/2 hr.	82.1	0.4	1/2 hr.	91.0
0.4	"	75.2	0.4	1 "	85.0	0.4	1 "	92.0
			0.4	24 "	86.0	0.4	24 "	93.1

It will be observed from Table II that a high initial concentration of H_2S in coal gas aids increased recovery of sulphur,

The efficiency of the reaction depends on the extent to which the intermixing of the reacting gases takes place. To aid this the reaction towers were packed with packing materials (spheres of marble of different diameters). These materials were so arranged as to leave about 40% of free space in them. Table III shows the result obtained with such modifications.

TABLE III

Velocity of reacting gases = 0.4 ft/min.

Proportion of H_2S by vol. in coal gas.	Interval after which the residual H_2S was estimated.	S deposited (% of total).	Proportion of H_2S by vol. in coal gas.	Interval after which the residual H_2S was estimated.	S deposited (% of total).	Proportion of H_2S by vol. in coal gas.	Interval after which the residual H_2S was estimated.	S deposited (% of total).
	Immediately	80.2		Immediately	84.1		Immediately	90.0
	1/2 hr.	80.4		1/2 hr.	84.7		1/2 hr.	91.6
1%	1 "	81.6	1.5%	1 "	85.2	2.6%	1 "	92.8
	24 "	82.2		24 "	85.9		24 "	94.5

Thus packing materials improved the %recovery to an appreciable extent.

Table IV embraces the results obtained by treating the coal gas mixture separately with nitrogen peroxide, and with a mixture of nitric oxide and nitrogen peroxide in proportions to form N_2O_3 . It will be evident from Table IV that much better results are obtained when nitrogen trioxide is used for precipitating the sulphur.

TABLE IV

Proportion of H_2S by volume in coal gas.	Interval after which the residual H_2S was estimated.	S deposited (% of total) with	
		NO_2 .	N_2O_3 .
	Immediately	94.7	96.8
	1/2 hr.	94.9	96.9
1%	1 "	95.3	97.2
	24 "	96.7	98.0

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ON THE MEASUREMENT OF THE ACTIVITY OF PROTEOLYTIC ENZYMES

BY NIRODE CHANDRA RAY

THE BENGAL IMMUNITY RESEARCH INSTITUTE, CALCUTTA

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The determination of the proteolytic activity of the enzymes—pepsin, papain and trypsin—is generally carried out by the estimation of the amount of substrate digested in a given length of time at a definite temperature, or by recording the time required to produce at a definite temperature a given change in the substrate. Among the physical and physico-chemical methods refractometric¹, nephelometric², viscometric³ and polarimetric⁴ methods are often followed.

But none of these methods specifically indicate the type of the enzymatic activity. Willstätter's method⁵ of evaluating the increase in amino-acids, employed in the measurement of enzymatic activity, actually measures both the proteinase and the peptidase activity. Fuld-Gross's method⁶ of estimating the amount of enzyme, which digests a known amount of substrate, measures only the proteinase activity of the enzymes. All the physical and physico-chemical methods, except the nephelometric one which indicates only the proteinase activity of an enzyme, measure the total activity of both (protease⁷ activity) of the proteinase and peptidase, or any one of the two. A comparison of the proteolytic activity of the different enzymes will have no significance unless the type of the enzymatic activity is taken into consideration.⁸ The nephelometric method, of course, is a quick and handy process for determining the proteinase activity within certain limits. The temperature and period of reaction of the enzymes, and the substrate are also to be considered. This temperature and period of reaction adopted by different authors^{1-6,8,9,12} range from 20° to 50° and from 10 minutes to 6 hours respectively, and the substrates used are also not all alike.

The proteinase and the peptidase do not act equally well at all temperatures. It is found that at high temperature the activity of the proteinase is more pronounced than that of the peptidase, while at lower temperature reverse is the case¹⁰. Further, all proteins are not digestible to the same extent by a particular enzyme. The increase in amino-acids in different substrates, caused by an enzyme at a definite temperature and period of reaction, may not therefore be equal and equitably comparable. The method of Anson¹¹ for the estimation of proteinase activity of pepsin, papain, trypsin etc., with denatured haemoglobin as substrate, goes to remove this anomaly, at least as regards the

substrate. He chooses the reaction temperature of 25° and the period of reaction for 10 minutes. But this temperature would not be so suitable in a tropical country and it would be difficult to obtain¹² standard preparations of haemoglobin.

Among other chemical methods, Fuld-Gross's method⁹ which takes casein (Hammersten), the most easily available protein, in normal caustic soda solution as substrate, is very simple and quick and can be adopted as a routine method in a day to day analysis, as it requires no special chemicals or appliances for reproducible results. But as in preparing the substrate according to Fuld-Gross, the casein solution is heated to the boiling point, certain changes in the composition of the protein may take place. Recently Bauer and White¹³ have found difficulty in reading the end-point of the digestion by using casein substrate in Fuld-Gross's method, and this has led him to adopt a method which estimates the total activity of both the proteinase and the peptidase, whereas in the U. S. P. XII⁹ the method of determination of the enzymatic activity in question is based on the measurement of the proteinase activity only.

Accordingly, an investigation was undertaken to find out an easy and simple method of measuring the proteolytic activity of the enzymes—pepsin, papain and trypsin. In the body of the paper the activity has been measured in terms of the proteinase activity using a specially prepared casein¹⁴ as substrate and digesting at 40° for 30 minutes. It may be recorded here that the difficulty, as experienced by Bauer and White¹³, may, of course, be avoided if only care be taken while adding the protein precipitant so that the clear solution in the test tubes may not be disturbed, when a well defined white ring with a slight turbidity in the upper zone is formed showing the presence of undigested protein.

EXPERIMENTAL

In the course of this investigation the following changes were made in adopting the Fuld-Gross's method for estimating the proteinase activity of the enzymes :

- (i) The reaction temperature was 40°.
- (ii) The digestion period was fixed for 30 minutes.
- (iii) The substrate casein was purified from industrial casein, under conditions (*vide infra*) which would allow the least chance of any chemical change in the casein. This casein¹⁴ is an improvement over the Hammersten variety^{15, 16}. Hammersten's method makes no specific recommendation for control of p_H and there is thus the danger of stopping short of p_H 4.6 during acidification and of redissolving in too strongly alkaline solution¹⁷.

The following criteria in the casein used were always adhered to : Moisture, 2.4% ; ash, 0.663% ; N₂, 13.95% ; Ca, 0.0293% ; P, 0.675% ; fat and lactose, nil.

Any alteration in the casein was guarded against by strictly limiting the p_H of the suspension at 6.3 and by working at the temperature of the refrigerator as far as possible. That the casein used in this investigation is not deteriorated during preparation is shown by its specific rotation $[\alpha]_D^{32} = -704$ at p_H 6.3 in aqueous solution, which is only 0.8% lower than that found by Winnick and Greenburg¹⁸. The substrates prepared with this casein are perfectly clear and are suitable for the purpose.

(iv) The substrate was prepared at room temperature.

(v) A slight modification as indicated in the procedure.

*Purification of Casein*¹⁴

Industrial casein (100 g.) was washed clean with tap water twice or thrice and finally with distilled water. The washed casein was then suspended in 1000 c.c. of distilled water and warmed¹⁹ to 80° in a boiling water-bath. The water extract was thoroughly decanted off and the process was repeated till the aqueous layer was colorless. To the aqueous suspension of casein, maintained at 55°-60°, a few c.c. of 2 *N*-NaOH solution were added to bring the casein quickly into solution (p_H not exceeding 8.0). Then *N*/100-HCl solution was immediately added, in quick succession, with constant stirring to bring the p_H of the suspension to 6.3. The suspension was quickly cooled and kept in the refrigerator for 24 hours, after adding a few c.c. of toluene and a few drops of chloroform and shaking well. The suspension was filtered next day through a tightly pressed filterpaper-pulp bed in a Buchner funnel. The *clear* filtrate was again cooled in the refrigerator, and it was then treated with *N*/100-HCl solution to bring the p_H to about 4.8; then the acid was added drop by drop, stirring all the while, till the casein was completely precipitated at p_H 4.6, and the whole was all the while kept cool by adding ice-chips. After one hour the casein was filtered through a four-fold muslin cloth and washed several times free of acid. The casein was then dried on a filter paper at room temperature and finally over sulphuric acid (conc.) in a desiccator. It was then finely powdered and stored in an airtight container away from light.

Preparation of Substrates

(A) *For pepsin*.—The purified casein (0.1g.) was weighed into a beaker and to it were added 20 c.c. of *N*/10-NaOH solution. The casein was dissolved at room temperature (25°-34°) within 10-15 minutes; the contents of the beaker might be warmed (not exceeding 34°) for a few minutes, if necessary. To the solution were then added 30 c. c. of *N*/10-HCl solution all at once. The solution was filtered through a filter paper into a 100 c. c. volumetric flask. The filter paper was washed thoroughly and the wash taken into the flask. The volume of the filtrate was made up to 100 c. c. The p_H of this *clear* solution is about 2.3.

(B) *For papain and trypsin.*—The purified casein (0.1 g.) was weighed into a beaker containing 20 c. c. of $N/10$ -NaOH solution. The casein was dissolved at room temperature (25° - 34°) within 10-15 minutes, warming (not exceeding 34°) for a few minutes, if necessary. Then 1 : 100 glacial acetic acid was added dropwise (9 to 10 c. c.) to bring the pH of the solution to 7.0. The volume of the solution was made up to 100 c. c. after filtration through a filter paper.

Precipitants for the Undigested Protein

(i) *For pepsin substrate* : Saturated ammonium sulphate.

(ii) *For papain and trypsin substrate* : A solution made of 50 c. c. of 95% alcohol, 1 c. c. of glacial acetic acid and 49 c. c. of distilled water.

Procedure

(a) *Pepsin.*—To each of the six test tubes serially marked were added 2 c. c. of the 0.1% casein substrate. 0.5 c. c. of distilled water was added to the first test tube, 0.4 c. c. to the second and so on up to 0.1 c. c. to the fifth test tube. The test tubes plugged with cotton were immersed in a thermostat at 40° for 10-15 minutes. Without removing the test tubes from the thermostat, the pepsin test solution was then added to the test tubes in increasing proportions, e.g. 0.1 c. c. to the first, 0.2 c. c. to the second test tube and so on up to 0.6 c. c. to the sixth one. The contents of the test tubes were thoroughly mixed, plugged with cotton and kept immersed in the thermostat for exactly 30 minutes. At the end of the digestion, six drops (1 drop = 0.05 c. c.) of saturated ammonium sulphate solution were added to each of the test tubes and thoroughly mixed. The mixture was 9% saturation with ammonium sulphate which was found sufficient to precipitate the whole of the undigested protein. The test tube which just ceased to show any turbidity would give the amount of pepsin which digests 2 c. c. of 0.1% casein substrate at 40° in 30 minutes.

(b) *Papain and trypsin.*—Procedure for the estimation of papain or trypsin is similar to that of pepsin, with the exception that at the end of the digestion period, six drops of alcohol-acetic acid mixture (1 c. c. = 0.03 c. c.) were slowly added to each of the six test tubes, such that the contents of the test tubes may not be disturbed violently. The test tube which just ceased to show the white ring with a slight turbidity or haziness in the upper zone would give the amount of papain or trypsin necessary to digest 2 c. c. of 0.1% casein substrate under conditions as specified.

For proper reading of the end-point of the digestion, the enzyme solution is so diluted that the end-point may occur in the middle portion of the series of test tubes. In case of papain, the substrates may also be diluted to avoid undesirable precipitation during addition or digestion, which may be necessary, especially when the papain is of inferior quality.

Units of the Proteolytic Activity

The proteinase attacks only the true protein, whereas the peptidase reacts after the protein has been degraded to non-protein stage. The determination of the activity of proteolytic enzymes in terms of proteinase activity would be more in keeping with the above facts. The proteolytic enzymes are, of course, proteinous in nature and they are generally, associated with foreign proteins in addition to other substances, sometimes added as adjuvants or dilutants. Preparations of enzyme materials are consequently found in different states of purity. For the advantage of comparison of the proteolytic activity of the enzymes, one practical unit of this activity may be defined as the amount contained in one part by weight of the enzyme preparation that would digest one part by weight of the protein substrate to non-protein stage under standard conditions. The number of units in 1 g. of the enzyme preparation would then be termed as the "Enzyme value" ^{20, 21}. In case of liquid preparations the unit may be expressed as the amount contained in 1 ml. of the enzyme solution, which digests 1 g. of the protein substrate under conditions as specified and the enzyme value as the number of units per ml. The number of units $[U]_{cas}^t$ of the proteinase activity of the following preparations, as determined by the method described herein, are shown in the following tables: (U=number of units, t=temperature; cas=casein substrate, Alb=albumin). In Table I the casein values obtained have been converted into the standard albumin values $([U]_{cas}^{40^\circ} \times 151.52 = [U]_{Alb}^{40^\circ})$.

TABLE I

Enzyme preparations	Number of units.	$[U]_{Alb}^{40^\circ}$	$[U]_{Alb}^t$
	$[U]_{cas}^{40^\circ}$ Found.	Calc.	Claimed.
Stearn's pepsin*	66.6	10,091	10,000
Stearn's pepsin D.A.B. 5	0.832	126	...
Pepsin (Neochemical Corporation, N.Y.)	19.8	3,000	3,000
Wilson's pepsin N.F.	19.8	3,000	3,000
Wilson's pepsin	66.0	10,000	10,000

*This sample has been used for comparing the number of units of the enzyme in terms of casein and albumin substrate

TABLE II

Enzyme preparation.	$[U]_{cas}^{40^\circ}$	$[U]_{cas}^{40^\circ} \times 7.$	$[U]_{Alb}^t$
	Found.	Calc.	Claimed.
Papain (Ceylon)	13	91	90
Papain (G)*	14	98	...
Papain (G.T.)	7.2	50.4	...
Papain (Ac)	0.5	3.5	...
Papain (S.B.P.)	1.1	7.7	...

*This sample of white papain has kindly been supplied by Dr. K. V. Giri of Bangalore.

TABLE III

Preparations of enzyme.	$\left[\text{U} \right]_{\text{cas}}^{40^\circ}$ Found	$\left[\text{U} \right]_{\text{cas}}^{40^\circ}$ Claimed (U.S.P.)
Pancreatin U.S.P.	26	25

Commonly this number of units of the activity of the enzyme powder is expressed as the ratio : one part by weight of the enzyme material is to parts by weight of the protein substrate. As for example, the B. P. pepsin is 1 : 2500 (albumin substrate) ; the U. S. P. Pancreatin is 1 : 25 (casein substrate) etc.

S U M M A R Y

A modification of the Fuld-Gross's method has been made for the determination of the proteinase activity of the proteolytic enzymes—pepsin, papain and pancreatin or trypsin. The determination of the proteolytic activity in terms of proteinase activity is advocated. The number of units of this activity or the enzyme value is expressed in terms of casein substrate for the proteolytic enzymes. Comparison of the 'enzyme value' of the preparations of proteolytic enzymes may very advantageously, be carried out by this method. The method is simple as well as quick and gives reproducible results.

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PREPARATION OF ACTIVATED CARBON FROM RICE-HUSK. PART II. ACTIVATION BY CARBONISING IN VARIOUS GAS ATMOSPHERES AND SECONDARY GAS ACTIVATION

BY J. K. CHOWDHURY, K. M. CHAKRABORTY AND J. K. GHOSH
APPLIED CHEMISTRY SECTION, DEPARTMENT OF CHEMISTRY, DACCA UNIVERSITY

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Activity of primary carbon prepared by heating various salt-impregnated rice-husks is greatly enhanced by secondary activation in gaseous atmospheres, particularly in carbon dioxide and compares favourably with imported varieties.

Work on preparation of activated carbon from rice-husk by impregnation with various inorganic salts has been published in a previous paper¹. The present work was directed to study the effect of various gas atmospheres during carbonisation. Also the carbon obtained by primary activation by the foregoing processes was subjected to secondary gas-activation. The nature and extent of the carbon produced were studied by various standard methods. An appreciable increase in activity resulted, though the increase in activity was not of the same nature.

Blayden *et al.*² carbonised Whatman's ashless filter paper (hydrochloric acid and hydrofluoric acid extracted) in presence and absence of an atmosphere of hydrochloric acid. They noticed that in a hydrochloric acid atmosphere, the increased yield amounted to nearly 100%, and in fact, almost reached that theoretically possible. In the present case, husk was carbonised in the acid atmosphere to study its effect towards the yield and activity of the resulting carbon.

Secondary activation of the carbons, obtained by some of the foregoing methods, was done using carbon dioxide and steam separately. In these experiments, temperature, time of activation and rate of gas-flow were changed to obtain previous condition for activation. The final gas was collected and analysed in order to throw some light on the nature and extent of the reactions involved.

EXPERIMENTAL

The raw material studied was the same as described in the previous paper¹ being sampled also in an identical way.

Methods of Testing the Activity

The carbon obtained in each case was thoroughly washed, dried at 105°, powdered and sieved through 100 mesh sieve and tested for its adsorbing capacity of (a) iodine (b) acetic acid and (c) methylene blue, as was done

before. In this case, however, methods of testing were extended to alkali and carbon tetrachloride vapour adsorption in order to ascertain if the acid or alkaline atmospheres during carbonisation had any effect in increasing the acid or alkaline property towards adsorption. The details of these two latter methods are given below, the other tests being made in the same way as was described in the previous paper.

Alkali test.—N/2-caustic soda solution (50 c.c.) was shaken with activated carbon, powdered to 100 mesh for 3 hours, and allowed to stand overnight. The solution (10 c.c.) was taken through a cotton filter and titrated against standardised acid solution. The total amount of unadsorbed alkali was thus determined and the amount adsorbed was expressed in mg./g. of activated carbon.

Carbon tetrachloride adsorption test.—A vessel containing carbon tetrachloride, kept at a temperature of 35-36° on a water-bath, was connected with a U tube containing 1g. of granular carbon, which was followed by a porcelain tube packed with pieces of pumice and heated strongly by a burner flame. Carbon tetrachloride was chased by dry air from an aspirator bottle passed at a constant rate of about 2.5 c.c. per minute. When the carbon was saturated with CCl_4 vapour, it passed through the hot porcelain tube where it was decomposed and the chlorine liberated a blue colour at once in the KI solution containing starch kept in a gas-washer and connected to the exit end of the porcelain tube. The flow of air through the CCl_4 was stopped as soon as the blue colour appeared. Under the experimental conditions, the quantity of CCl_4 adsorbed was calculated from the initial and final weight of the 'U' tube and the result was expressed in mg./g. of the activated carbon.

Carbonisation in various Gas Atmospheres

(a) *Hydrochloric acid gas.*—Gaseous hydrochloric acid was obtained from Kipp's apparatus by the action of moderately concentrated sulphuric acid on ammonium chloride pieces and was dried by passing through a gas-bottle containing H_2SO_4 (conc.). The dried gas was then passed through a silica tube, at the centre of which dry rice-husk was packed between two asbestos plugs for carbonisation. The tube was heated in an electric furnace. Sufficient 'hydrochloric acid' gas was passed through the reaction tube to chase off the last trace of air. The electric current was next started to raise the temperature of the tube. The carbon obtained was, as usual, refluxed with hydrochloric acid and finally washed to remove the last trace of acid and dried at 105° in an electric oven. The carbonisation was continued at 350°, 400° and 450°. The time of activation was later varied to 4 hours and 8 hours at 450° which showed optimum activity for 6 hours of activation-time. The data are given in Table I.

TABLE I

Dry husk taken = 7.85 g.

Temp	Time.	Yield	Adsorption (in mg./g.) of activated carbon			Alkali.
			Iodine.	Acetic acid.	Methylene blue.	
350°	6.0 hrs.	53.0%	133	26	27	51
400°	6.0	55.6	168	41	200	63
450°	6.0	52.4	272	44	200	67
450°	4.0	59.0	152	32	100	73
450°	8.0	44.0	272	47	200	66
Blank test (carbonisation in ordinary conditions).						
400°	6.0	42.4	282	14	160	...

From Table I the iodine activity appears to have deteriorated in comparison with the primary carbon obtained in the ordinary way, whereas the acetic acid and methylene blue activities have increased in appreciable extent. It is also obvious that considering both yield and activity of the resulting carbon, prepared under the above different conditions, carbonisation at 450° continued for 6 hours yielded the best product.

(b) *Carbonisation in ammonia atmosphere.*—It was thought interesting to study, for comparison, the behaviour of the carbon obtained by carbonising in an alkaline atmosphere, for which purpose ammonia gas was chosen. It was obtained by dropping liquor ammonia on caustic soda beads and dried over quick lime. Here also, the conditions were kept the same as were in the case of HCl gas-atmosphere, but later the time of carbonisation was varied at 350° which was considered to be the best for ammonia atmosphere.

TABLE II

Dry husk taken = 7.85 g.

Temp.	Time.	Yield.	Adsorption (in mg./g.) of activated carbon.			Alkali.
			Iodine.	Acetic acid.	Methylene blue.	
350°	6.0 hrs.	51.2%	569	26	250	112
400°	6.0	43.7	381	26	181	90
450°	6.0	42.3	232	30	213	64
350°	4.0	52.0	598	24	259	106
350°	8.0	50.0	579	39	254	123
(Blank)						
400°	6	42.5	282	14	160	...

Evidently, iodine and methylene blue activities are considerably increased by carbonisation in ammonia atmosphere, particularly at 350° and continued for 4 hours, but considering the yield and activity in general, product on 8 hours' heating is thought to be the best. From the above data of alkali and acid adsorption, it clearly indicates that the carbon derives a basic character

[when obtained by carbonising in an acidic atmosphere, whereas, a basic atmosphere imparts an acidic character to the carbonised mass.

(c) *Carbonisation in an atmosphere of nitrogen, steam and carbon dioxide.*—Next the carbonisation was studied in the atmosphere of nitrogen which is more or less an inert gas. Nitrogen was obtained by the action of sodium nitrite and ammonium chloride. For purification, it was passed through ferrous sulphate and caustic soda solutions, washed with water and finally dried through sulphuric acid.

Steam, carbon dioxide and their mixtures are generally used for secondary activation. This study here, however, was made to note their behaviour in course of primary activation. Steam was passed through a silica tube heated strongly from outside before it was introduced to the carbonisation tube. Carbon dioxide was obtained from a Kipp's apparatus, and as usual, was washed and dried before use.

TABLE III

Dry husk taken = 7.85 g. Temp. = 400°. Time = 6 hrs.

Atmosphere.	Yield.	Adsorption (in mg./g.) of activated carbon.		
		Iodine.	Acetic acid.	Methylene blue.
...	42.5%	282	14	160
Nitrogen ...	41.8	208	26	120
Steam ...	87.0	168	11	76
Carbon dioxide ...	43.0	193	17	120

It is observed that none of the above gases have any appreciable effect to justify their use during primary activation and in fact, the activity of the resulting carbon is poorer than that of the carbon obtained in the ordinary way.

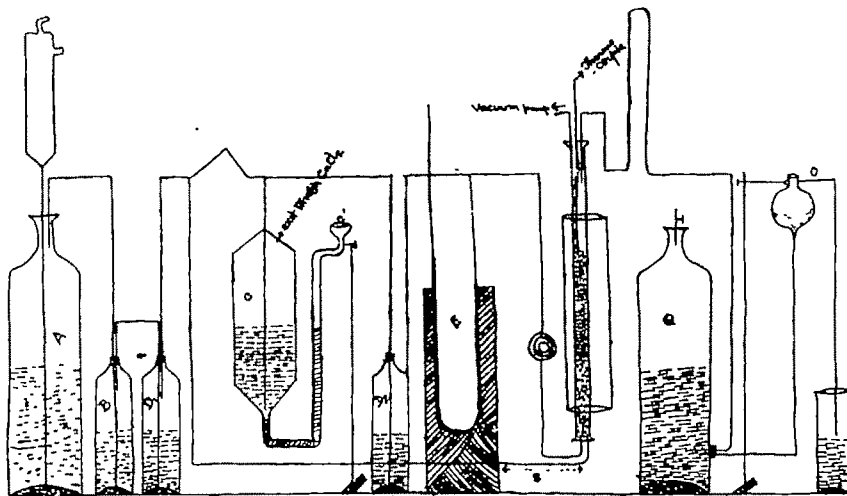
Secondary Activation of Carbon by Steam and Carbon Dioxide

In consideration of the high yield and activity of carbons, obtained by some of the foregoing processes, attempt was next made to increase the activity by secondary activation in a current of carbon dioxide and steam separately. The conditions were varied in turn to get the optimum condition for maximum activity. Experimental arrangement and procedure are described below. In all these experiments, 3 g. of the primary carbon were taken in each charge. The temperature for activation was varied between 500° and 1000°, time between 5 and 40 minutes and the rate of flow of carbon dioxide between 2.19 and 6.57 c.c. per minute at N. T. P.

Arrangement for gas-activation by carbon dioxide.—The set up of the apparatus is shown in Fig. 1. CO₂ was collected in the aspirator bottle A and forced through the wash-bottle B, D₁ and D₂ into the reaction tube R

by the pressure of water column A_1 . Wash-bottle B contains water to wash off any free acid that might be present and D_1 and D_2 contain sulphuric acid to dry the gas. In C, glycerine stands at a certain level which could be adjusted by leveling the reservoir C. E is the manometer containing liquid paraffin which indicated the difference in pressure. The rate of passing

FIG. 1.

*Arrangement for CO_2 activation.*

the gas could be obtained with sufficient accuracy by counting the number of bubbles passing through the wash-bottle D_2 per minute. The rate could be maintained constant, for a slight increase in pressure would push down glycerine level in the inner tube in C and the gas would escape through it, thereby releasing the pressure immediately. Lowering in rate would be indicated by a rise in the level of liquid paraffin in the manometer tube E. The resulting gas was collected in the aspirator bottle G at a constant pressure, the displaced water escaping through a constant level outlet O. Since activation in a current of CO_2 deteriorated the adsorbing capacity, if continued for a long time, temperature of the primary carbon was raised from room temperature to the temperature of activation in vacuum. The primary carbon was taken in the centre of a glazed porcelain tube and was introduced into the resistance furnace. The temperature was read by means of a thermocouple- P, placed inside the reaction tube touching the primary carbon. The reaction tube was next connected to a vacuum pump. When the manometer read a pressure of 3 mm. of mercury, the heating current was turned on, the vacuum pump being in action during the heating period. When the desired temperature was reached, connection with the pump was cut off and the carbon dioxide was admitted into the reaction tube through a capillary tube S to avoid sudden rush of gas. On reaching the atmospheric pressure, this passage was cut off and the gas was allowed to flow through the regular passage and the time recorded.

Table IV shows the results of a set of experiments where temperature was kept constant, time of activation and the rate of flow of gas being varied.

TABLE IV

Secondary activation of carbon obtained by carbonising the husk at 450° for 6 hrs. in the atmosphere of HCl gas by CO₂.

Charge = 3 g. Temp. = 500°.

Time. (min.)	Rate*	Yield**	Adsorption (in mg./g) of activated carbon.				Gas collected [†] .	Analysis of gas,	
			Iodine.	Acetic acid.	Meth. blue.	CCl ₄ .			
—	—	—	272	44	200	47	—	—	—
5.0	2.19	90.1%	386	102	200	96	21.0	80.9%	17.2%
10.0	„	89.5	419	143	210	83	41.0	81.2	16.7
20.0	„	88.0	438	129	200	82	82.0	82.8	15.8
30.0	„	87.0	438	129	200	74	128.0	83.0	15.8
40.0	„	86.0	419	116	200	69	177.0	82.9	15.9
5.0	4.38	88.0	422	123	200	44	21.0	88.0	9.0
10.0	„	85.0	422	123	210	41	40.0	87.8	9.2
20.0	„	85.0	394	129	210	38	100.0	87.9	9.2
5.0	6.57	93.0	381	108	246	42	41.6	92.3	7.3
10.0	„	90.6	351	116	246	49	82.0	92.0	7.4
20.0	„	86.0	351	84	200	44	102.0	88.0	27.0

*In c. c. per minute at N. T. P.

**With respect to primary carbon taken.

†In c. c. in room temperature and pressure

According to expectation, the yield of carbon gradually decreases with the time of activation. Activity with respect to iodine, acetic acid and CCl₄ adsorption reaches a maximum under certain conditions, deviation from which causes a decrease of activity, while methylene blue activity remains more or less the same. Here also it is observed that certain conditions which increase one particular kind of activity do not necessarily increase or decrease it with respect to any other kind or in other words, certain defined conditions for activation are best for one purpose but not for all. When compared with respect to the activity of initial carbon (prior to secondary activation) we find that acetic acid activity increases enormously and iodine and carbon tetrachloride activities also increase appreciably. Increase in the gas flow rate does not help to justify it³ except in the case of methylene blue activity which increases a little with the rate of flow. In general however, flow rate of 2.19 c.c. per minute was considered best and the activating temperature was next varied keeping the time constant at 10 minutes.

TABLE V

Secondary activation of carbon obtained by carbonising the husk at 450° for 6 hrs. in an atmosphere of HCl gas.

Charge—3 g. Time—10 mins.

Temp.	Rate* -	Yield**	Adsorption (in mg./g.) of carbon.					Analysis of gas.	
			Iodine.	Acetic acid acid.	Meth. blue.	COCl ₄ .	Gas collected.	CO ₂ .	CO.
—	0	—	272	44	200	47	—	—	—
500°	2.19	89.5%	419	148	210	88	41.0 c.c.	81.2%	16.7%
600°	„	90.0	358	84	225	77	60.0	68.2	27.1
700°	„	90.0	395	87	210	42	70.0	61.9	29.2
800°	„	87.3	381	84	182	57	78.0	61.0	35.0
900°	„	91.5	189	21	200	43	68.0	51.4	49.8
1000°	„	94.4	127	15	210	40	70.0	46.8	50.0
(x)	„	91.8	97	15	225	44	134.4	46.8	51.2

*In c.c. per min. at N. T. P.

**With respect to primary carbon taken.

(x) Activation was continued for 20 mins. instead of 10.

Table V shows that the yield gradually decreases as the temperature is increased from 600° to 800° above which the yield increases again decreasing the adsorbing capacity of the resulting coke. The reason does not seem to be clear though a possible explanation is that at that high temperature carbon had the structure of graphite, this causing reduction in its activity. It does not, however, explain the increase in yield. At first, it was thought that the ash fused at that temperature lowering the activity, but actual test showed that the fusion point of the ash was much higher. In the above table it is seen that decrease in activity sets on at 800° which suddenly accelerates at 900°. The methylene blue and carbon tetrachloride activity undergo very slight change within long range. From the ratio of carbon dioxide to carbon monoxide in the gas collected, it can be well understood that the nature of the reaction changes in the vicinity of 900° when CO₂/CO ratio is about 1 instead of about 2 at a lower temperature range.

In the next set of experiments, primary carbon obtained in the ammonia atmosphere, carbonised for 8 hours at 350°, was subjected to secondary activation by carbon dioxide.

A rate of 2.19 c.c./min was preferred as it was found most suitable in the former case. In general 10 minute's time of activation yielded better results at 500° and 600° and hence at higher temperatures activation was continued for 10 minutes. In this case also yield decreased with temperature at the lower range, while at about 800° it gradually began to increase. Compared with the activity of primary carbon, the iodine activity decreased considerably,

TABLE VI

Charge = 3 g.

Rate of flow = 2.19 c.c. per minute at N. T. P.

Temp.	Time. (min.)	Yield	Adsorption (in mg./g.) of carbon				Gas collected.	Analysis of gas.		
			Iodine.	Acetic acid.	Meth. blue.	CCl ₄ .		CO ₂ .	CO.	CH ₄ .
...	0	0	578	39	254	44	...	0 %	0 %	0 %
500°	5.0	92.9%	255	60	210	29	25.0 c.c.	81.5	13.3	5.1
..	10.0	89.9	295	72	213	33	45.0	81.4	13.5	5.0
600°	5.0	87.6	266	66	200	32	40.0	76.2	16.5	5.0
..	10.0	86.9	312	84	234	24	76.0	76.4	16.8	5.3
700°	10.0	83.1	231	60	168	29	80.0	57.8	38.5	5.0
800°	10.0	84.0	178	42	200	31	80.0	55.2	40.0	4.8
900°	10.0	85.0	117	15	210	40	82.0	50.3	48.2	5.1
1000°	10.0	88.0	89	11.3	222	53	85.0	45.8	48.2	5.0

whereas acetic acid activity decidedly increased. An appreciable quantity of hydrocarbon was found in the gas collected and given in the table estimated as methane. This probably originated from the adsorbed ammonia in the primary carbon which was not liberated even under vacuum at the high temperature.

Carbon dioxide activation was next tried on primary carbon obtained from husk impregnated with ammonium phosphate prior to carbonisation. The sample in question was impregnated with 10 c.c. of saturated solution of ammonium phosphate (7.85 g. of dry husk), carbonised at 450° for 4 hours. Secondary activation was continued for 10 minutes at a rate of 2.19 c.c./min.

TABLE VII

Carbon from husk carbonised at 450° for 4 hrs. by impregnating with ammonium phosphate.

Charge = 3 g. Time of activation = 10 mins. Rate of gas flow = 2.19 c.c./min. at N. T. P.

Temp.	Yield.	Adsorption (in mg./g.) of carbon				Gas collected.	Analysis of gas.	
		Iodine	Acetic acid.	Meth. blue.	CCl ₄ .		CO ₂ .	CO.
—	—	425	54	153	86	—	—	—
500°	93.0%	446	240	340	181	34 c.c.	82.3%	16.5%
600°	91.0	226	66	240	128	38	55.2	48.4
700°	89.4	164	35	225	108	33	55.08	45.3
800°	83.3	127	15	225	104	34	46.2	53.8
900°	81.9	116	15	218	95	36	46.2	53.8
1000°	79.8	84	10	210	84	36	43.7	57.0

Unlike the two previous cases, yield of the carbon decreased continuously throughout the whole range, and the volume of the gaseous products collected was comparatively much small and remained practically constant though CO_2/CO ratio changed. Iodine activity remained almost unchanged when activation was carried at 500° , beyond which it decreased continuously. A spectacular increase in acetic acid and methylene blue activity was noticeable also in the 500° product which also decreased continuously with rise in temperature. In this set of tests also, the sudden change in activity synchronised with the sudden change in the reactivity of the primary carbon with respect to the reaction with carbon dioxide. For example, at 500° CO_2 in the resulting gas was 5 times that of CO by volume, whereas at 600° , the CO content was only a little less than that of CO_2 . CCl_4 activity increased appreciably.

The behaviour of primary carbon obtained by carbonising the husk for 4 hours at 450° , pretreated with ammonium borate, was next studied.

TABLE VIII

Charge = 3 g. Time of activation = 10 mins. Rate of gas flow = 2.19 c.c. per min. at N. T. P.

Temp.	Yield.	Adsorption (in mg./g.) of carbon				Gas collected	Analysis	
		Iodine.	Acetic acid.	Meth. blue.	CCl_4 .		CO_2 .	CO .
—	—	474	46	153	132	—	—	—
500°	92.2%	495	60	213	214	46 c.c.	78.3%	21.8%
600°	88.9	489	90	206	197	56	68.5	31.2
700°	85.3	480	84	200	143	60	71.2	27.04
800°	86.6	457	72	186	73	68	62.5	36.0
900°	87.4	286	60	177	62	68	51.2	46.9
1000°	90.7	258	42	168	53.8	66	50.7	47.6

Here also the yield decreased until 700° and from 800° it increased again. No sudden change in activity was noticeable in this case, so also in CO_2/CO ratio of the resulting gas. The 500° product showed best activity with respect to iodine, methylene blue and carbon tetrachloride adsorption, although appreciable increase was noticeable only in the latter two.

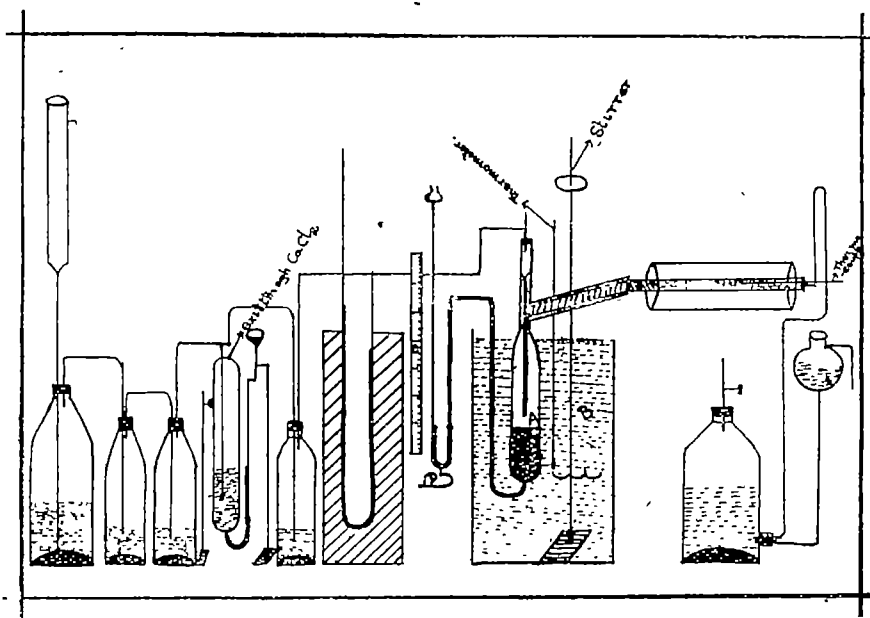
Activation by Steam

Secondary activation was next studied using a steady uniform flow of steam chased by nitrogen. The steam entering the reaction tube was passed through a strongly heated column of broken pieces of alundum tube and thereby became superheated, before reaching the primary carbon.

The apparatus employed for passing steam through the primary carbon for activation is shown Fig. 2. Water vapour, generated in vessel A, was chased by nitrogen, previously dried by passing through sulphuric acid at a constant rate. Purified nitrogen was stored in an aspirator bottle. The vessel A

containing redistilled water was kept immersed in a big water-bath B. The level of water in vessel A, which could be read from the scale C attached to the 'U' tube in syphonic connection with A. At the beginning of each experiment, water was brought to the same level. The temperature

FIG. 2

*Arrangement for steam activation.*

of the water-bath could be kept constant within 0.05° by passing a constant current through electrical immersion heaters used for raising the temperature. The water lost from the bath due to evaporation in course of experiment was continuously supplied from a reservoir, so that the mass remained practically constant. To avoid condensation of water, the glass tube connecting A with the reaction chamber was electrically heated. The bath temperature and the rate of passing nitrogen through A remaining constant, a definite amount of water vapour would be chased per minute. The moisture carried on was determined by absorption in a 'U' tube containing calcium chloride. The data are given below.

TABLE IX

Rate of flow = 2.19 c. c./min. Time = 20 mins.

Bath temp. = 80° .Bath temp. = 90°

Water absorbed by CaCl_2	Mean,	Water absorbed by CaCl_2	Mean.
0.0104 g.	} 0.0108 g.	0.0156 g.	} 0.0155 g.
0.0102		0.0155	
0.0108		0.0154	

The following table shows the data obtained by steam-activation of primary carbon in HCl-atmosphere.

TABLE X

Charge = 3 g. Time = 10 mins. Rate of steam passed = 0.00077 g./min.

Temp.	Yield.	Adsorption (in mg./g.) of carbon				Gas collected.	Analysis of gas.		
		Iodine.	Acetic acid.	Methylene blue.	CCl ₄ .		CO ₂ .	CO.	H ₂ .
...	...	272	44	200	47
500°	95.0%	293	126	161	95	80 c.c.	18.18%	38.0%	22.0%
600°	93.4	317	135	173	125	80	18.0	26.0	24.0
700°	90.0	358	112	161	187	98	6.0	23.0	50.0
800°	82.0	317	89	161	120	104	5.0	29.0	45.0

No test above 800° was made as it would only decrease the activity. Increase in carbon tetrachloride activity is conspicuous, being maximum at 700°, which also corresponds to the highest iodine activity. Increase in acetic acid activity is considerable compared with the initial activity. As is expected, CO and H₂ contents of the gas increase with temperature originated from water-gas reaction, simultaneously increasing the total volume of gas collected. It is evident that steam-activation has advantage over CO₂-activation with respect to CCl₄ activity, but is decidedly inferior with respect to all other activities. Steam activation was next tried on primary carbon obtained in ammonia atmosphere, and the results are given in Table XI

TABLE XI

Secondary activation by steam.

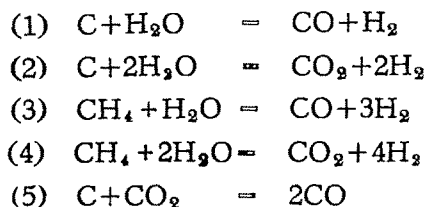
Primary carbon was obtained by carbonising the husk at 350° for 8 hours in ammonia atmosphere.

Charge = 3 g. Time of activation = 10 mins. Rate of steam passed = 0.00077 g. per min.

Temp.	Yield.	Adsorption (in mg./g.) of carbon				Gas collected.	Analysis of gas.			
		Iodine.	Acetic acid.	Meth. blue.	CCl ₄ .		CO ₂ .	CO.	H ₂ .	CH ₄ .
...	...	578	39	254	44
500°	92.0%	285	65	173	53	80 c. c.	6.0%	23.0%	40.0%	14.0%
600°	88.0	288	95	199	155	86	9.8	24.0	40.0	8.0
700°	85.0	271	89	173	121	95	7.8	27.0	39.0	6.1
800°	78.0	251	58	161	98	101	7.0	28.0	35.0	6.5

It is noticeable that the iodine activity has been considerably lowered by the treatment and in general, though the data indicate definite increase in

acetic acid and CCl_4 activities, it is rather small and does not justify the process. The resulting gas contains hydrocarbons in appreciable quantity. The hydrocarbon content suddenly drops at 600° after which it is almost steady. This can be explained by supposing that part of the CH_4 formed is instantaneously acted on by steam at a temperature of 600° and above, resulting, in more oxides of carbon and hydrogen. The probable reactions were:—



More complex reactions between adsorbed ammonia in the primary carbon and the red hot carbon with the formation of hydrocarbons and nitrogen are also likely.

Steam-activation was then tried on primary carbons obtained by impregnating with the inorganic salts, where appreciable increase in activity was noticed in the primary stage. The results obtained in this way on ammonium phosphate-treated primary carbon is reproduced in Table XII.

TABLE XII

Steam activation on primary carbon obtained by carbonising husk at 450° for 4 hours pretreated with ammonium phosphate.

Charge = 3 g. Time of activation = 10 mins. Rate of steam passed = 0.00077 g. per min.

Temp.	Yield.	Adsorption (in mg./g.) of carbon.				Gas collected.	Analysis of gas,		
		Iodine.	Acetic acid.	Meth. blue.	CCl_4 .		CO_2 .	CO.	H.
...	...	425	54	153	85
500°	86.9%	453	69	241	160	40 c. c	20%	14%	26.4%
600°	85.6	419	62	213	120	50	13	13	25.0
700°	84.11	358	58	199	105	70	15	18	35.0
800°	84.7	261	56	173	87	80	19	23	37.0

Obviously, highest activity was obtained at 500° and higher temperature resulted in a gradual decrease. Compared to the primary carbon, methylene blue and carbon tetrachloride activity is considerably increased.

TABLE XIII

Steam activation on primary carbon by carbonising the husk at 450° for 4 hours pretreated with ammonium borate.

Charge = 3 g. Time of activation = 10 mins. Rate of steam passed = 0.00077g. per min.

Temp.	Yield.	Adsorption (in mg./g.) of carbon.				Gas collected.	Analysis of gas.		
		Iodine.	Acetic acid.	Meth. blue.	CCl ₄		CO ₂ .	CO.	H.
...	...	476	47	153	132
500°	78.8%	469	112	199	148	180 c c.	5.0%	29.0%	40.0%
600°	74.9	469	126	199	212	180	8.0	30.0	46.0
700°	74.4	445	126	183	185	180	5.5	38.0	50.0
800°	73.3	398	103	161	121	180	6.0	34.0	57.0

Compared to primary carbon, considerable increase in CCl₄ and acetic acid activity was obtained. When carbon dioxide and steam are compared as activating agents, it can be observed that carbon dioxide is much more active than steam. In all cases of gas activation, maximum activities were obtained using either 500° or 600° as reaction temperature. Higher temperatures only caused decrease in activity. It is to be noticed that carbon obtained from ammonium borate treatment is very reactive with steam as is evident from the data in Table XIII causing low yield of carbon and high amount of gas formation. The gas formed remained constant at all reaction temperatures though the composition changed.

The following table is intended to compare the activity of two well known varieties of activated carbon, 'Norit' and 'Kahlbaum activated carbon'. Our best samples for iodine, methylene blue and CCl₄ activity proved to be much more active than either 'Norit' or Kahlbaum's carbon. Methylene blue activity is, however, higher in our sample than that of 'Norit' but less than that of Kahlbaum's carbon. Average activity compares favourably with both the imported samples. Acetic acid activity of our sample is particularly much higher.

TABLE XIV

Nature of carbon.	Condition of primary activation.	Secondary treatment with	Adsorption (in mg./g.) of activated carbon			
			Iodine.	Acetic acid.	Meth blue.	CCl ₄ .
Rice husk	Ammonia atmosphere for 4 hrs at 350°	—	598	24	259	—
"	Treated with phosphate at 450° for 4 hrs.	Carbon dioxide	446	240	340	181
"	Do.	"	"	"	"	"
"	Treated with Am. borate at 450° for 4 hrs.	"	495	60	249	214
"	Treated with Am. phosphate for 4 hrs at 450°	"	448	240	340	181
Norit			458	60	314	114
Kahlbaum's carbon			503	119	393	124

S U M M A R Y

1. Secondary activation considerably increases the activity of the primary carbon. This increase is of specific nature, *i.e.*, the treatment may increase the activity in one or more respects but not necessarily in all kinds and neither to the same degree. In fact in some cases decrease in activity is noticed in some respects.

2. Relatively high flow rate of the activating gas lowers its activating capacity.

3. A temperature range of 500° or 600° is most effective, depending on the process. Higher temperatures result in lower activity in all cases.

4. Carbon dioxide is a much better activating agent than steam.

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STUDIES IN GANGETIC SILT. PART I. ITS PROPERTIES WITH REFERENCE TO CERAMIC PURPOSE

BY CHITTAPRASAD DE, S. K. CHATTERJEE AND H. N. DAS-GUPTA

DEPARTMENT OF APPLIED CHEMISTRY, UNIVERSITY COLLEGE OF SCIENCE &
TECHNOLOGY, CALCUTTA

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The properties of the Gangetic silt have been studied with the reference to its use as a ceramic material.

The Gangetic silt has been in use as a ceramic material in some parts of India, particularly in Northern India where it serves as a profitable source for the manufacture of common pottery wares¹. It appears, however, that no work has been done with a view to obtaining informations leading to a better understanding of its properties. In the present paper an attempt has been made to study some of its properties which have a bearing on its utility in the manufacture of pottery wares.

The silt was collected from a number of overhead tanks for unfiltered water, situated at different localities in Calcutta, and an average sample was prepared for studying its properties. It may be pointed out that almost identical properties were observed with specimen, collected from the settling tanks of Palta Water Works

EXPERIMENTAL

The silt is grey in colour, possessing a specific gravity of 2.47. It is characterised by remarkably fine-grained texture. This property is most suitable for the formation of thin-walled bodies. By elutriation in water it is possible to separate the silt into five fractions of different sizes as shown in Table I.

TABLE I

Average diameter.	% by weight.	Average diameter.	% by weight.
0.006427 mm ...	15.06	0.02466 mm. ...	27.96
0.010690 ...	10.80	0.03311 ...	19.52
		0.04335 ...	27.16

Table II gives an approximate idea of the mineralogical composition of the silt as obtained from 'rational' analysis and Table III gives the result of ultimate analysis.

TABLE II

Free silica	...	27.7%	Carbonate of lime	...	8.0%
Clay substance	...	58.7	Limonite	...	8.8

TABLE III

SiO ₂	...	54.2%	Fe ₂ O ₃	...	9.8%	MgO	...	Slight trace
Al ₂ O ₃	...	22.4	CaO	...	5.01	Ignition loss		4.6%

From above it appears that the silt is a heterogeneous collection consisting of calcareous, ferruginous, siliceous and clayey materials.

Colloidal matter.—There is no satisfactory method for estimating the total colloid content of clay. The malachite green test for gauging the colloid content is due to Ashley². This test gives a measure of the absorptive power of the colloid present. In accordance with this test, silt (1 g.) absorbs 0.2662 g. of malachite green oxalate.

Sulphur compounds.—Usually, sulphur occurs in clay in three different forms, viz. (i) soluble sulphur, like sulphurous and sulphuric acids, some sulphides, sulphites, and sulphates, (ii) pyritic sulphur, and as (iii) sulpho-silicates. Of these, the pyrite is a very common form of sulphur. If, however, the proportion of pyritic sulphur be great, the inner core of the burnt ware is liable to contain black specks of undecomposed iron sulphide³. The silt, under investigation, however, contains a small percentage of sulphur compounds as will be evident from Table IV.

TABLE IV

Water soluble sulphur	0.0087%
Pyritic sulphur	0.009%
Sulpho-silicate	Nil

Softening point.—A small quantity of the material, made up into pyrometric cones, was subjected to the pyrometric cone equivalent (P. C. E.) test in the usual manner. Based on three trials, the softening point, expressed in terms of Seger cones, was between cones 3a and 4a.

Drying shrinkage.—This is an important property, as clay materials, having an excessive shrinkage, cause drying cracks, warpage, and distortion of the ware. Besides, a knowledge of both drying and firing shrinkage is essential in order to maintain the correct size and shape of the finished piece. The linear drying shrinkage of the silt is 7.69% by plastic length or is 8.3% by dry length. This value is quite good as the range of linear drying shrinkage varies between 0 and 15%⁴.

Burning shrinkage and behaviour in firing.—The burning shrinkage of clays varies between wide limits, as this depends on a number of factors, such as the kind of clay and its fineness, the proportion of organic material in them, process adopted in the formation of the body and the temperature of firing. In some clays the maximum burning shrinkage may be reached at a comparatively low temperature, while in others this is attained at higher temperatures. The burning shrinkage of the silt was determined in accordance with the method outlined for it and the following results were obtained

Linear burning shrinkage (up to 1120°)	...	8.5%
Volume " " " "	...	23.4%

Fig. 1 shows the relation of burning shrinkage to various heat treatment

FIG 1

FIG 2

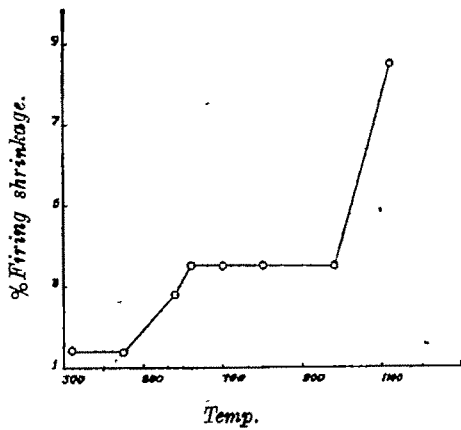


FIG 2A

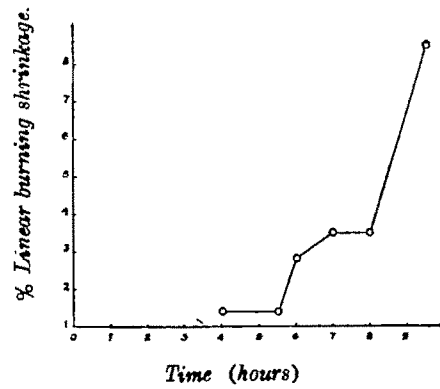
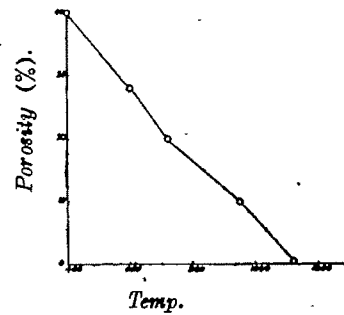
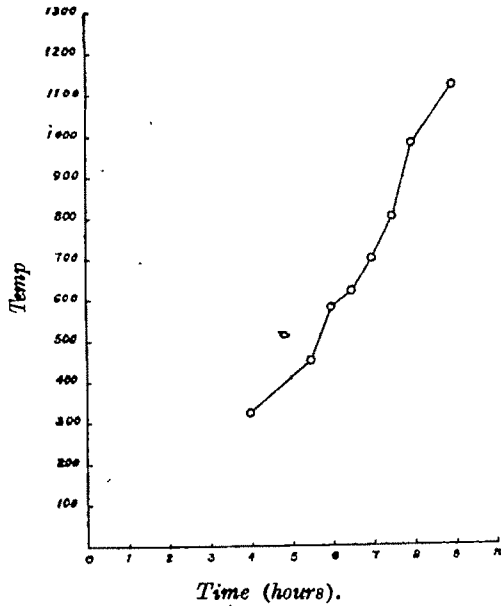


FIG 3



and figure 2 shows the relation of shrinkage to time. The rise of temperature

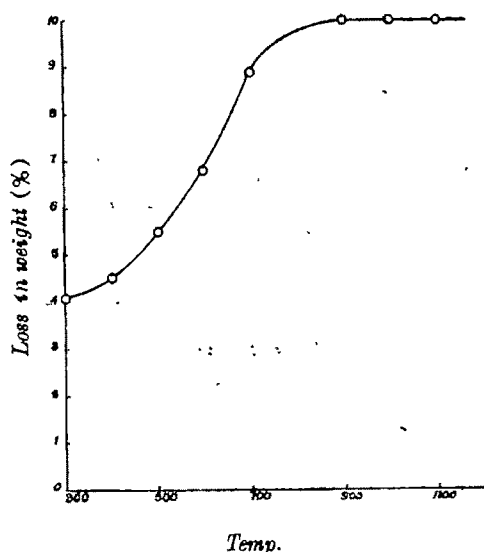
with time is not regular and this will be evident from Fig. 2A. It may be mentioned that temperature determinations were made with a thermocouple and not with pyrometric cones.

Apparent porosity.—This was determined at different temperatures in accordance with the method recommended by the American Ceramic Society⁶. Figure 3 shows the relation of porosity to various heat treatments.

The silt bodies on firing assume a dark red coloration. The apparent specific gravity of a burnt product is 2.6 and the true specific gravity is 2.7.

Loss in weight.—A trial piece, measuring two inches side, was made by pressing the silt. This was first dried till bone-dry and its weight noted. The

FIG 4



piece was next fired in an electric oven with slow rise of temperature, which was noted with a pyrometer. Figure 4 shows the loss in weight due to firing at different temperatures. It is interesting to note that the silt body loses its weight slowly up to 500° but between 500° and 900° the loss in weight is very appreciable and after that there is no further loss.

Ceramic possibilities.—From analytical results it is evident that the proportions of silica and alumina in the silt are quite reasonable but, it is high in iron oxide and lime and as such it is less refractory. This accounts for the reason why it is being used for the

manufacture of Terracotta and common earthen ware goods. The vitrification range of the silt is very narrow and hence the firing must be regulated very carefully. This defect, however, can be mitigated when suitable proportions of good fire-clay and grog, prepared from the silt itself, be mixed with the silt. A very satisfactory result was obtained by using the following composition :

Ganges body silt	...	80%
Fire-clay	...	15%
Fire grog	...	5%

The silt alone has a narrow range of firing. But the range of firing, with the above mentioned body composition, is fairly wide. When fired at 1000°, it gives a body with about 10% water absorption. The sp. gr. of the fired body is 2.69 and it gives a good sound.

As pointed out previously, articles, prepared from silt, produce dark red colour on being fired. This may be covered with a plumbiferous transparent glaze in which case a decorative effect may be obtained. In fact, articles for table top decoration may be prepared by using a transparent glaze. Bodies may also be coated with coloured glazes in order to conceal the colour due to excess of iron. A few tried recipes of lead enamels are given in Table V.

TABLE V.

	1.	2.	3.	4.		1.	2.	3.	4.
Red lead	65	63	60	62	Antimony oxide	4
Quartz	22	24	20	22	Ferric oxide	0.5
Felspar	8	4	6	4	Black stain	1	...
Tin dioxide	...	3	4	0.5	Silt	5	5
Cobalt oxide	...	1	China clay	...	5	5	...

No 1 is transparent; 2, blue; 3, black; 4, yellow. Black stain suitable for this may be prepared from manganese dioxide 4 parts, cobalt oxide 2 parts and copper oxide 2.5 parts. The glazes mature at temperatures varying between 975° and 1025°.

It is also possible to apply a white raw opaque glaze to silt wares. For this purpose the following recipes are quite satisfactory.

	Body	Glaze		Glaze.		
Silt	75 parts	White lead	...	35 parts	Kaolin	... 3 parts
Fire-clay	20	Felspar	...	28	Tin dioxide	... 12
Grog	5	Whiting	...	10	Flint	... 12

The glaze matures at 1030°. The appearance of the resulting product is fairly white and the articles may be passed for fine earthen wares.

For obvious reason it is not ordinarily possible to get white wares from silt. Lime has a well known bleaching effect on the red colours of iron⁶. It makes the fired body whiter. Usually more than 5% lime is not recommended for this purpose as it tends to lower the firing range of the body. With the silt, however, a buff coloured product was obtained, using 5% lime. When, however, 10% of lime was used the fired product was nearly white. But with such a high percentage of lime great care need be exercised in firing the body and this is not feasible commercially.

The real remedy lies in removing the iron and not in suppressing the iron colour. In fact, some successful experiments had been done by some workers in order to remove iron from clay by converting the iron into volatile ferric chloride. At present a solution of basic aluminium chloride has found wide

application⁷. A number of experiments, as enumerated below, were undertaken to examine the possibility of removing the iron from the silt and thereby to make the same suitable for the production of fine earthenware bodies.

Definite proportions of silt were mixed separately with different chlorides or sulphates or both, and each mixture was either pressed into a bar and heated very slowly to different temperatures, or it was made into a slurry for autoclaving or steaming purpose. In each case the residual iron content of the treated product was estimated after thorough washing. Table VI shows the effect of such treatment.

TABLE VI

Bleaching agents used.	Mixture made into	Maximum temp.	Duration.	% Fe ₂ O ₃ removed.
Aluminium chloride (crystal)	Bar	1000°	10 hrs.	4.8
Salt and aluminium hydroxide	"	1000°	11	5.6
Basic aluminium chloride	"	950°	6	5.2
Ammonium chloride	"	200°	4	10.2
Ammonium chloride and alum	"	190°	3	24.6
Do	Slurry	Autoclaved at 1.5 to 2 Kilos	3	28.7
Do	"	Steaming	3	10.7
Aluminium chloride and alum	"	Autoclaved at 1.5 to 2 Kilos	3	39.3
Ammonium sulphate	Bar	190°	3	49.2

It is thus obvious from the table that the silt can be bleached only to a limited extent.

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STUDIES IN GANGETIC SILT. PART II. ITS USE IN OIL REFINING

BY S. K. CHATTERJEE AND H. N. DAS-GUPTA

DEPARTMENT OF APPLIED CHEMISTRY, UNIVERSITY COLLEGE OF SCIENCE &
TECHNOLOGY, CALCUTTA

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Gangetic silt has been activated and its adsorptive and bleaching properties studied.

In order to bleach vegetable, animal and mineral oils, fats and waxes, bleaching earth, prepared by chemical processing of clays, is being extensively used at present¹. Clay, suitable for activation, varies from green, yellow to grey in colour. From this point of view it was considered desirable to activate the Gangetic silt. The results, so far obtained, have been included in the experimental portion.

EXPERIMENTAL

The silt was subjected to activation process in accordance with the procedure outlined by Burghardt¹. Dry silt (100 g.) was mixed with sufficient water to form a thick slime. This slime was next treated either with hydrochloric acid or with sulphuric acid (100 c. c., 1 : 1) and live steam was passed through the mixture to raise its temperature to boiling. The duration of steaming varied between 3 and 5 hours. After steaming the mass was filtered, washed free of acid, and then dried. The dried product was ground to pass through 150 mesh sieve but retained on 200 mesh sieve. Part of the ground product was subjected to a temperature of 400°, and the bleaching properties of the two were separately determined. For the sake of comparison the bleaching power of both raw and activated silt was studied.

In order to test the adsorptive capacity of the silt for acid or alkali, each specimen (1 g.) was stirred with 25 c. c. of *N*/10-NaOH or acetic acid for one hour and the quantity of alkali or acid adsorbed was determined in the usual way. Table I shows the results obtained.

TABLE I

Specimen.	Weight adsorbed from	
	NaOH soln.	Acetic acid soln.
1. Raw silt	0.0046	0.00021
2. Silt activated by HCl	0.016	0.0086
3. Activated by HCl & calcined at 400° for $\frac{1}{2}$ hour	0.02	0.0044
4. Activated by H ₂ SO ₄	0.0142	0.008
5. Activated by H ₂ SO ₄ & calcined at 400° for $\frac{1}{2}$ hour	0.0194	0.00395

Clarification of Oils

Oils listed in Table II were treated separately with bleaching earth at 84°-85° for $\frac{1}{2}$ hour in the usual way. After filtration the colour of the clear oils was determined by a colorimeter. These results are incorporated in Table II

TABLE II

Oil treated.	Silt activated by	Extent of colour removed.	Oil treated	Silt activated by	Extent of colour removed.
	HCl	32%			
	H ₂ SO ₄	38	Linseed oil	Hydrochloric acid	32.4%
Groundnut	HCl & calcined at 400°	47.4	Neem oil	Hydrochloric acid	37.5
				Sulphuric acid	37.9
	H ₂ SO ₄ & calcined at 400°	46.9			
	Raw silt	10.7	Kerosene	Hydrochloric acid	43.5
				Sulphuric acid	38.2

From Table II it is clear that the bleaching effect is pronounced when the activated silt is calcined. Table III shows the effect of temperatures on the bleaching power of silt, activated by hydrochloric acid.

TABLE III

Calcined at	...	85°	220°	400°	500°	900°
Extent of colour removed (%) from groundnut oil		32	38.2	48.1	47.9	47.9

From Table III it is clear that temperature above 400° is not favourable for increased activity.

Silt, activated by hydrochloric acid, was treated for half an hour with different oils at 84°-85° in order to determine the extent to which the acid value was altered. These results are included in Table IV.

TABLE IV

Oil treated.	Extent of colour removed.	Acid value original.	Acid value final	Oil treated.	Extent of colour removed.	Acid value original.	Acid value final.
Maize	35.5%	19.2	17.8	Neem	37.5	20.4	17.6
Linseed	32.4	15.0	14.4	Castor	41.8	24.6	23.04
Groundnut	47.8	23.8	20.2	Coconut	47	11.6	9.7

The sulphuric acid liquor, left after activating the silt, was used again with a view to testing its efficacy in activating a fresh quantity of silt. It was found that there was very little deterioration in its activating power. This will be evident from Table V.

TABLE V

Oil treated	Extent of colour removed.	Remarks.
Castor	43.1	
Coconut	40.5	
Neem	33.8	
Groundnut	47.1	Calcined at 400°
Coconut	41.1	Do

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STUDIES IN COLLOIDAL GRAPHITE. PART I. PREPARATION¹ OF COLLOIDAL GRAPHITE IN WATER FROM INDIAN RAW MATERIALS

BY K. K. MAJUMDAR

DEPARTMENT OF METALLURGY, INDIAN INSTITUTE OF SCIENCE, BANGALORE
(Received April 28, 1948)

Colloidal graphite in water was first prepared by Acheson¹ by grinding a mixture of graphite and tannic acid. The colloidal suspension was stable in presence of ammonia, but was rapidly coagulated by acids. In order to concentrate the product Acheson and his co-workers² proposed to pass the solution through a filter having a surface or filling of rubber. Townsend³ suggested to remove water from colloidal suspensions by precipitating colloidal graphite with acetone, methyl or ethyl alcohol. The precipitated graphite could be dried in warm air and dispersed in water readily. In a later patent⁴ Acheson mentioned the use of canvas-covered rolls for deflocculating graphite. He also indicated the possibility of using products obtained by roasting rice, corn, etc., and extracting with ammonia. He found⁴ that the moisture content of paste during grinding should be about 24 to 27%. In order to concentrate the product, Acheson⁴ later on patented the use of acids for precipitating the colloid, the coagulated mass being reprecipitated with infusion of hay or straw. Patents⁵ have also been taken by Karplus, Hatschek, Pigache, and others. Recently Lyuten⁶ has reviewed the processes so far adopted. He found that neutralised sulphite liquor is a very good stabiliser.

EXPERIMENTAL

Purification of natural graphite.—Samples of natural graphite from different parts of India were subjected to purification by froth flotation in Ruth cells. Almost all samples responded to flotation and could easily be purified to 95% carbon content. Crystalline graphite from East Godavari area was purified to about 98% carbon by using potassium xanthate as collector, eucalyptus oil as frother and maintaining the p_H of the pulp between 8 and 9. The purified graphite was dried and then roasted in saggers in an inert atmosphere at about 1200° to drive off volatile matter and for making the mass porous. This treatment facilitates grinding.

Grinding and purification of graphite.—Various grinding aids like naphthalene, sugar, etc., were tried for fine pulverisation without success. The material was finally ground in a mill, similar to Raymond mill, fitted with air separator. Finely powdered graphite was collected from the bag.

With a powerful electro-magnet, iron particles from the ground graphite were removed and then the latter treated with hydrochloric acid to dissolve the ash, whereby the purity was increased to 99%.

Preparation of colloid.—Colloidal graphite was prepared by grinding purified, pulverised graphite with about 25% of its weight of sodium oleate in a triple roller mill. No other grinding mill was found suitable for this purpose. The grinding was continued for a few hours and distilled water was added from time to time to keep the mass pasty. The colloidal particles, which were formed due to attrition, were immediately coated with the protective colloid. The pasty material was then transferred to a tank, thoroughly mixed with distilled water, and then allowed to sediment for 6 to 7 days. Centrifuging could not be attempted for the volume of suspension was fairly large. After a few days, the colloidal solution, free from coarse particles, was syphoned off, and the colloidal material coagulated with a minimum quantity of hydrochloric acid. The coagulum was collected by sedimentation and was again mixed with about 10% of its weight of sodium oleate and a little alkali and ground for sometime in the triple roller mill. It was then kept in air-tight bottles.

Preparation of colloidal graphite in water with tannic acid, gelatine etc., was not successful. The colloid so prepared readily dispersed in water and was fairly stable towards acids.

S U M M A R Y

Colloidal graphite in water was prepared from Indian graphite by grinding purified graphite in presence of protective colloids like sodium oleate. The coarser particles were separated from the colloids by the dilution of the mass and sedimentation. The colloid was concentrated by coagulation with mineral acids, and the coagulum peptised by grinding with more protective colloid and a little alkali.

The author's thanks are due to Sir J. C. Ghosh, for providing facilities for carrying on the above investigations and for helpful suggestions.

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ON THE CHARACTERISTICS OF INDIAN OX-BILE POWDER

BY SUKHAMOY BHATTACHARYA AND U. P. BASU.

THE BENGAL IMMUNITY RESEARCH INSTITUTE, CALCUTTA

(Received June 8, 1948)

Bile salts are now-a-days largely used in medicine and for this the raw gall-bladder bile, as available from the local slaughter houses, is to be processed either for the isolation of sodium tauroglycocholate or for the production of sodium dehydrocholate. It has been previously recorded from this laboratory¹ that Indian ox-bile is not always of uniform quality. Recently it has again been noted by Basu and Ray² that the refractive indices and other physical properties of the bile, collected from the gall bladders of slaughtered animals, indicate that more than 20% of the animals do not often afford bladders rich in good quality bile.

India is a vast country and transport difficulty arises in collecting liquid bile under refrigerating conditions from different centres to any centralised production unit. As such it would be better if the bile be concentrated to solid consistency, suitable for its easy and rapid transport. It has already been shown² that such a product retains all the characteristics of bile salts. In the present paper further studies have been made on the properties of the bile powder that has been obtained by concentrating the gall-bladder bile from different slaughter houses in India; and a standard for the bile powder has been suggested.

EXPERIMENTAL

Samples have been received both as bile paste and as solid cake. The bile pastes were evaporated to dryness and powdered. This powder as well as the cake were subjected to the following tests.

Ash and sulphated ash were determined in the usual way.

Estimation of total bile acids.—For this 0.5 g. of bile powder, accurately weighed, was heated with 30 c. c. of 15% caustic soda solution under reflux for 12 hours and the hydrolysed product was treated exactly in the way as described in the assay of sodium tauroglycocholate in British Pharmaceutical Codex³. The final weight of the ethereal extract gave the total bile acids.

Acid value of total bile acids.—The liberated acid in the estimation of total bile acids was dissolved in alcohol (95%) and the volume made up to 25 c.c. in a volumetric flask. A 10 c.c. portion was titrated against standard

TABLE I
Characteristics of ox-bile powder.

Sample	No.	Ash.	Sulphated ash.	Total bile acid.	Cholic Acid ^a .	Yield of pure cholic acid.	7% solution pH	Ref. Index.	Acid value of bile acids.	$[\alpha]_D$ of bile acids.
Bile, solid	1	12.52%	20.60%	65.00%	68.9%	—	7.5	1.3433	135.1	+ 27° at 31.5°
"	2	9.44	17.72	58.30	58.2	22.30%	—	—	132.1	+ 31.2° at 27°
"	3	12.04	18.84	61.90	—	24.01	7.3	1.3438	—	+ 30.7° at 28.5°
"	4	8.20	17.76	59.30	57.6	23.10	7.1	1.3425	133.0	—
"	5	10.20	18.10	59.50	58.1	23.20	7.2	1.3440	133.8	+ 32.3° at 27°
"	6	12.56	20.00	66.85	65.5	24.30	7.6	1.3435	134.3	—
"	7	13.40	18.87	64.20	61.0	27.80	6.6	1.3436	130.0	+ 30.92° at 28.5°
Bile, paste (solid content 64.8%)	1	12.90	20.18	71.50	68.3	30.00	7.55	1.3445	130.8	+ 28.15° at 28°
(solid content 61.5%)	2	11.05	20.42	68.30	69.3	22.40	7.8	1.3455	139.0	+ 33.05° at 31°
(solid content 67.5%)	3	13.93	19.66	63.08	61.2	—	7.6	1.3435	133.1	+ 30.03° at 26.5°
Cholic acid **									131.2	+ 33.98° at 27°
Reference standard cholic acid U.S.P.									136.72	+ 36.47° at 27°

^a Calculated from the acid value of the total bile acids in terms of cholic acid.

** Prepared in this laboratory.

decinormal caustic potash using phenolphthalein as the indicator. The results are expressed as the number of mg. of caustic potash per g. of the bile acid.

Specific rotation $[\alpha]$ *of total bile acids*.—A portion from the alcoholic solution of the liberated bile acids in the acid value estimation was used for the determination of specific rotation of the acid using Schmidt and Haensch polarimeter. In average 1 to 1.5% solutions of the bile acid were made for determining the above values. The specific rotation for cholic acid was found not to alter to any appreciable degree with the above change in concentration.

Refractive index, η , and p_H .—As it has been previously found (Basu *et al.*¹) that average solid content of bile comes to about 7% of the liquid, a 7% solution of the powder, or cake was made in distilled water. The refractive index of the solution was determined by an Abbe refractometer and the corresponding p_H was determined by a Beckmann glass electrode p_H -meter. Measurements were taken at room temperature varying from 27° to 35°.

Yield of pure cholic acid.—Cholic acid was isolated and purified according to the method of Gattermann⁴.

The results of these experiments, calculated on solid basis, have been recorded in Table I. The table also contains the acid value and specific rotation of a cholic acid isolated and purified in this laboratory as well as those of a U. S. P. cholic acid (Reference standard), 1942 for comparison.

The average, maximum and minimum values of the characteristics of bile powder are compiled in Table II.

TABLE II

Average characteristics of bile powder

	Ash,	Sulphated ash,	Total bile acid,	p_H †	Refractive index *	Acid value of bile acids	$[\alpha]_D$.
Maximum	13.93%	20.06%	71.5 %	7.80	1.3455	189.0	+33.05°
Minimum	8.20	16.87	58.3	6.60	1.3426	180.0	+27°
Average	11.62	19.01	63.79	7.36	1.3438	133.5	+30.8°

* of 7% solution.

DISCUSSION

The acid values of bile acids isolated from different samples, as well as the specific rotation do not appear to vary appreciably from pure cholic acid. The averages of the various characteristics have been recorded in Table II

along with the maximum and minimum. As such any powder having the characteristics as laid down in Table III may be considered to be suitable for the production of bile salt or bile acid derivatives.

TABLE III

Suggested standards for ox-bile powder

	Sulphated ash.	Total bile acids.	pH of 7% solution.	Ref. index of 7% soln.	Acid value of bile acids.	Specific rotation.
Limit	17-21%	Not less than 58%	7-8	1.3425 to 1.3455*	Not less than 130	Not less than 270*

* at 80°.

SUMMARY

1. Various characteristics of Indian ox-bile after drying it to solid powder have been determined.
2. A standard for solid bile powder, suitable for the production of bile salt or bile acid derivatives, has been laid down.

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NOTES & NEWS

Unveiling of the Portrait of Acharya Prafulla Chandra Ray

A portrait of the late Acharya Prafulla Chandra Ray, the Founder President of the Indian Chemical Society, was unveiled by H. E. Dr. K. N. Katju, Governor of West Bengal.

The ceremony was held on August 2 (which coincides with Sir P. C. Ray's birthday) at the instance of the Indian Chemical Society at the University College of Science, Calcutta.

The President of the Society, Prof. P. Rây, in course of his welcome address said "Prafulla Chandra Ray was the pioneer of chemical researches and chemical industries in India, who laid the foundation of the Indian School of Chemistry. Great as he was as a scientist and a teacher, he was greater still as a man: for, we found in him a great social reformer, a great philanthropist and a great patriot, who identified himself with the sorrows and joys of his fellow countrymen, and who lived the ideal life of the ancient Indian sages based on simplicity, service and sacrifice. He was one of those few towering personalities of the last generation, who awakened India from her long intellectual inertia and placed her on the path of progress and enlightenment. It was through his inspiration, both spiritual and material, that the Indian Chemical Society came into existence some twenty-five years ago. He was not only our Founder President but was also elected President for two terms; and almost to the end

of his life he remained our friend, philosopher and guide. It was, therefore, with a deep sense of gratitude and reverence that the Indian chemical Society opened, soon after his death, a fund with a view to perpetuating the memory of his services. Contributions to this fund were received mainly from our Fellows, our supporters and from the pupils of the late Acharya Ray; we received little or no help from the general public or from the Government; our efforts failed even to gain any publicity in the nationalist press. As a result, our collection fell far short of expectation and did not exceed even Rs. 12,000/- in all. Fortunately, however, the P. C. Ray 80th Birthday Celebration Committee, through the earnest and untiring efforts of Prof. M. N. Saha, came to our rescue. They made over their entire collection of about Rs. 30,000/- to us, which has enabled us to inaugurate this memorial lecture to-day. I take this opportunity of expressing our thankfulness to the Birthday Celebration Committee; and to Prof. M. N. Saha in particular, for their generous help and ungrudging co-operation in the matter. Finally, I would like to offer our most grateful thanks to his Excellency, the Governor of West Bengal, who, inspite of the pressing demand of manifold official and social duties on his time, was very kind enough to accept our invitation and is here with us to-day to perform the Unveiling Ceremony. This is an indication not only of his regard for the late Acharya Ray, but also of his

interest in the activities of our Society. I welcome his Excellency not only because he is the Governor of a province, but because he is one of our great national leaders, who, like Acharya Ray, has lived a simple life of service and sacrifice".

Dwelling on the life and work of Sir P. C. Ray, H. E. Dr K. N. Katju said "Acharya Ray was without doubt one of our few great men who were produced during the last 100 years. He led the life of a true Brahmachari. He was like a true grand-father; he has left behind him thousands of spiritual descendants who would worship his memory so long as they lived. And after them for centuries his name will remain enshrined in the history of national India.

"He had really the most wonderful personality closely resembling Gandhiji in a variety of ways. He was noted for his austerity and simplicity. Acharya Ray was not merely a scientist, he was a great patriot with profound knowledge of science, coupled with the great devotion to his spinning wheel.

"Acharya Ray, was an extremist in every way. As a man he was the most modern, most advanced and most learned scientist that the age could produce, while on the other hand he was the greatest spinner who wanted to identify himself with the poorest of the people, and also identify himself with the greatest struggle for national freedom which the world has ever seen in recorded history. In between there was no single activity in which he did not associate himself. Whenever the call of the country came, whenever the floodstricken wanted relief, the poor

and the sick called for help, there was Acharya Ray in the forefront always helping them, rushing to their assistance"

The portrait was executed by Sri S. N. Bagchi.

Inauguration of Sir P. C. Ray Memorial Lecture

The first Sir P. C. Ray Memorial Lecture, founded by the Indian Chemical Society, was delivered at the University College of Science, Calcutta, on August 2, 1948.

The President of the Society invited Prof. N. R. Dhar to deliver his lecture with the following words :—

"Professor Nilratan Dhar of the University of Allahabad needs little introduction to this assembly. So far as the Indian Chemical Society is concerned, he is one of us; for, he is not only a Foundation Fellow and a Past-President of the Society, but he is also one of our Vice-Presidents now. Besides, the Indian Chemical Society received at one time a substantial material help from him. The selection of Prof. Dhar as the first P. C. Ray Memorial Lecturer has got a special significance of its own. For, among the pupils of the late Acharya Ray, nobody can possibly claim closer association with the great master in his private, public and scientific life than Prof. Dhar; and nobody can possibly excel him in his love and admiration for the great teacher. If any evidence be needed, I may refer here to his princely donation of Rs. 200,000/- to the University of Calcutta—practically his life's savings—

for founding a Professorship in the name of his Guru, Acharya Prafulla Chandra Ray. The Council of the Indian Chemical Society, therefore, on the recommendation of the Memorial Lecture Committee, rightly decided that their first public homage to the illustrious soul should be paid through a high priest, who is best fitted for the task by his devotion and loyalty to his Guru. In this, I believe, Professor Dhar stands second to none. With blessings and encouragement from his great Guru, Prof. Dhar started his career as a pioneer of physico-chemical researches in India, and succeeded in catalyzing and fertilizing many young minds with the fascinating ideas of this branch of our science. The votaries of Physical Chemistry in India to-day will remain indebted to Prof. Dhar for this great service rendered by him. Prof. Dhar is going to speak this afternoon on "Nitrogen transformation in Nature", a subject on which he has been working for several years and in which he has made notable contributions. This is a subject, which is closely related to the problem of nutrition and food, a problem for the solution of which the late Acharya Ray worked and preached throughout his life, and published several booklets and articles on the same. This problem, as you are aware, has assumed a vital importance for us all to-day, and, I am sure, you must be eager to hear from Prof. Dhar the results of his long-standing researches on the subject. Without, therefore, standing any longer between you and our learned lecturer, I have now the greatest pleasure in inviting Prof. Dhar to deliver his lecture.

Prof. Dhar speaking on "Nitrogen transformation in Nature" demonstrated through simple laboratory experiments the comparative ineffectiveness of fertilizing available land with inorganic nitrogen substance. Below is given a brief summary of the lecture.

Nitrogen Transformations in Nature. All living substances contain nitrogen as one of its ingredients and hence the supply of nitrogenous matter for plants and animals is perhaps the biggest problem of humanity. Neither most plants nor animals can utilize the free nitrogen present in air in building up their bodies. There is an essential difference between animals and plants depending upon the fact that plants can thrive on simple inorganic nitrogenous substances like ammonium salts, nitrates for their nitrogen requirements, whilst animals must have complex organic compounds containing not only nitrogen but also carbon, hydrogen, oxygen and frequently sulphur and phosphorus for their existence. These substances are known as amino-acids and proteins.

Between the two great world wars, the modern powers had established the nitrogen fixation industry for manufacturing ammonium salts and nitrates. This industry at present is as important as the coal or steel industry. A small part of these inorganic compounds of nitrogen is utilized as manure even by the advanced nations for improved food production. The majority is utilized for explosives and other industrial operations. Researches carried on at Allahabad and elsewhere have definitely established that when ammonium

salts are added to the soil as a manure, a large proportion is not utilized by the crop nor it remains in the soil but is wasted as nitrogen gas. Moreover, it has been proved that inorganic manures do not improve the fertility of the soil permanently as organic manures like cow-dung, farmyard manure, plant residues, leaves, molasses etc., are capable of doing. Rothamsted results obtained from experiments lasting for a century have shown that when even 100 lbs. of nitrogen are added per acre in the form of ammonium salt or nitrate, it does not improve the nitrogen content of the soil permanently, but with farmyard manure at the rate of 14 tons per acre the nitrogen content of the soil is increased 300 per cent. This has been explained from the researches carried on at Allahabad University because organic matter leads to nitrogen fixation from air and the protection of soil nitrogen. It is clear therefore that it is not absolutely necessary to add inorganic or organic nitrogenous manures to the soil for crop improvement but energy producing organic substances not containing any nitrogen like molasses rich in carbohydrates, plant residues, straw etc., rich in celluloses can increase the soil nitrogen permanently by fixing the nitrogen of the atmosphere on the soil surface. The value of farmyard manure or cowdung depends not only on its nitrogen content, as it is generally believed, but on its ability to fix atmospheric nitrogen and thus enriching the soil. Rain water adds approximately 7 to 8 lbs. of nitrogen per acre of land in most parts of India and this is a useful source of nitrogen in a readily available form. Alluvial

soils of India contain approximately 1000 pounds of total nitrogen per acre of land up to 9 inches deep, whilst the soils in temperate climate contain approximately double the amount of total nitrogen, but due to the high temperature and sunlight prevailing in India, the amount of ammonium salts and nitrates which are known as available nitrogen and is actually used by growing plants in building up their body materials is approximately 100 lbs. per acre, whilst in colder countries it is 20 lbs. A good crop of wheat or paddy requires 30 to 40 lbs. of nitrogen per acre. This explains why a steady crop yield is observed in most tropical countries even without the addition of any artificial manures. The cellulose materials remaining in the soil after harvesting the crops cause nitrogen fixation which is aided by sunlight and this is the chief source of the constant supply of nitrogen in tropical agriculture. Researches at Allahabad have shown that more nitrogen is fixed by the help of sunlight on the surface of the Earth than the total nitrogen fixed in all industrial concerns of the world. The source of soil nitrogen is the fixation of nitrogen of the air on soil surface by the oxidation of cellulosic and other organic substances.

Plants can synthesise complex organic compounds like starch, proteins from simple inorganic substances aided by sunlight. These products, prepared by plants, are utilized by human beings for their existence and doing work. Modern researches have established that the amount and quality of the protein prepared by plants vary a great deal with the variety of the plant. Moreover,

the amino-acids obtained from proteins have been divided into two groups known as essential and non-essential amino-acids. The essential ones are absolutely necessary for the growth of human body and maintenance of health. The proteins available in animal food materials like milk, fish, eggs, meat contain more essential amino-acids than in plant proteins and hence it is absolutely necessary for building of body and brain power that some animal protein has to be consumed. Yeast, which is manufactured in Europe and America at a small cost, is rich in essential amino-acids and vitamins and is an excellent food material especially for poor people who have to depend upon cheap vegetable proteins. It is interesting to note that although wheat is richer in the total protein and vitamin contents than rice, which is the staple food of the Eastern nations, the protein of rice, however, is much richer in essential amino-acids than the wheat proteins. It appears therefore that the good quality protein present in rice is the chief source of the brain power of the Eastern nations and that is why rice is so largely cultivated in the oriental countries.

Standard on Quality Control

For the benefit of manufacturers in India, the Indian Standards Institution has reprinted the American War Standard Z 1. 3.—1942, on the "Control Chart Method of Controlling Quality during Production" (price Rs. 3/8/-). The method described in the standard details the statistical procedure to be adopted during inspection of samples,

the interpretation of data and application of results, leading to well co-ordinated and most economic utilisation of raw materials and labour in industry, and to significant improvements in the quality of finished products.

This publication, which incidentally is the first issued by the Indian Standards Institution, is intended to help Indian industrialists to save in wastage of materials, to increase production of quality products and generally to place every industry on a sound competitive basis. Copies can be had from the Secretary, Indian Standards Institution, P Block, Raisina Road, New Delhi.

In view of the immediate need for making a suitable publication available for the use of manufacturers in this country, the Sectional Committee on Quality Control and Industrial Statistics appointed by the Indian Standards Institution recommended a reissue of the American Standards on this subject, while the Committee is engaged on the time-consuming task of compilation of an Indian Standard more closely suited to Indian conditions.

The Quality Control technique in Industry was first originated in the U. S. A., and has since been effectively adopted in Britain, Canada and Australia. Dr. W. A. Shewhart, the American expert on Quality Control, who recently visited this country at the joint invitation of the Indian Statistical Institute and the Indian Standards Institution, inspired much enthusiasm for adoption of modern Quality Control methods in Indian Industries, which

are now at the beginning of a bright era of expansion and development.

That India has begun to realise the need for Quality Control methods is evidenced by the activities of the recently established Indian Society for Quality Control, and the establishment of a training course in Statistical Quality Control in Bombay by the Textile Association (India).

Cosmic Ray Investigations in Pacific

An important contribution to knowledge of cosmic ray phenomena is expected to follow investigations now being made in Pacific area by Mr. Phillip G. Law, who was the leader of the scientific team that accompanied Australia's recent Antarctic expedition.

During his four month's voyage in Antarctic waters he collected some highly interesting data on the intensity of cosmic rays around the South pole. As the intensity of cosmic rays varies according to latitude and conditions of temperature and pressure, Mr. Law will now compare the results he obtained in Antarctica with readings taken on and north of the equator. Cosmic rays intensity is highest at the earth's poles, and the effect on the intensity by the earth's magnetic field is greatest at the equator.

Mr. Law has installed his Geiger telescopic counter equipment aboard H. M. A. S. Duntroon—an Australian troopship that runs between Sydney and the British Commonwealth Occupation forces in Japan. The route of the Duntroon provides ideal conditions for Mr. Law's investigations.

Very little is known about cosmic rays although it has been established that they bombard the earth from outer space. The rays consist of particles which travel into the earth's atmosphere at velocities infinitely greater than those that scientists could ever hope to produce in the laboratory. As the cosmic ray particles strike the earth's atmosphere they "bump" into other particles normally present in the atmosphere. Because of their terrific velocity the cosmic rays disintegrate the comparatively slow moving atmospheric particles.

Thus, if science can gain a good knowledge of the nature of cosmic rays the disintegration of matter or "splitting" of the atom can be studied under conditions much better than can be achieved with cyclotrons in the laboratory. (Len Barker, No. P/911)

Exchange of Scientific Knowledge : Australian Interest in India

The visit of an Australian Goodwill Scientific Mission to India this year may lead to a regular exchange of students and scientists between the two countries. The mission has already recommended that a party of Indian scientists be invited to visit Australia.

"The visit of the delegation should be the forerunner of much closer scientific contacts between India and Australia and Pakistan and Australia," said the Secretary (Mr. G. B. Gresford) in a report on the visit recently issued. "At a later date, when conditions are more normal, it should be possible to arrange for the

accommodation of a number of students from these two countries to carry out post-graduate work in Australia, and for the exchange of workers between the Council for Scientific and Industrial Research in Australia and the Council for Scientific and Industrial Research of India. In the meantime it is proposed to recommend that a group of scientists be invited to Australia to return the visit paid by this delegation."

Members of the delegation received a large number of enquiries from Indian students about the possibility of undertaking work, particularly post-graduate study, in Australian Universities.

"The various difficulties Australian Universities would experience at present in accommodating Indian students, due to over-crowded post-war conditions, were explained to the enquirers. Nevertheless, it is apparent that a demand is likely to arise from Indians to study in Australia, and the delegation feels that when conditions become more normal this should be encouraged.

"The exchange of students at an impressionable age would be very useful in building up goodwill between the two countries", the report continued. "Members of Indian university staffs also enquired about the possibility of visiting Australia for short periods for lecturing or research purposes and about the possibility of arranging exchanges. The detailed method of carrying out such suggestions would involve many difficulties, but it is felt that everything should be done to encourage exchange wherever possible." There is no doubt that in the academic world India is looking to Australia as a friend. (N.B. ; R. No. P/910).

Adhesives from Castor-seed Protein

Protein, extracted from castor-seed cake by water, common salt solution, varying concentrations of NaOH or Na_2SO_3 , is precipitated by HAc or HCl or H_2SO_4 . Proteins as obtained are admixed, either in wet or in dry condition with different proportions of ammonia, formalin and either borax or tri-sodium phosphate. The feasibility of utilising the adhesives, thus prepared, in the manufacture of plywood has been investigated. Tests have been performed with 3/16" Hollock* (*Terminalia Myriocarpa*) boards under different conditions of temperature and pressure. It is finally concluded that these adhesives are not as good as those obtained from groundnut protein as far as manufacture of commercial plywood is concerned. (Indian Forest Leaflet, No. 100).

Absorptiometry

Of the modern methods of instrumental analysis absorptiometry has found widest application in almost every phase in inorganic analysis and also in many aspects of organic analysis. Absorptiometry is an improvement on the older method of colorimetric analysis where the intensity of colour produced by modern organic reagents on elements is measured photo-electrically. (*Chem. Age*, 1948, No 1511).

Automatic Water-hardness Tester

Permutit Co., Ltd., have placed on the market, a simple, reliable instrument for automatic determination of residual

hardnes in softened water treated in base-exchange water-softeners.

The instrument is coupled to the softener by a small-bore tubing. The test-result is signalled by lamps or a mechanical indicator. A buzzer, included in the instrument, gives warning when 'hard' water passes through the exchanger and thus the moment for re-generation is indicated. Under normal working the instrument needs refilling with soap solution at monthly intervals. The current consumption is stated to be negligible. (*S. P. C. May*, 1948).

Aerosol

Insecticides when used in aerosol form are more effective than when used as a wet-spray. The superiority of aerosol is due to the minuteness of the liquid-particles (10 to $.25\mu$) compared to that of wet spray ($1/25$ to $1/100$ inch). The minutely sized particles of aerosol can remain in suspension for a long time, in still air and will not burst in contacting a surface which is therefore not wetted as would otherwise happen in the case of wet spray. The aerosol particles also possess Brownian movement, and are highly diffusive and permeative. Another distinctive advantage of this system is that there is no fire-hazards from aerosol of inflammable liquids such as kerosene. On an average one pint of a suitable insecticide in aerosol form is usually sufficient to destroy all insects in a space up to 30,000 cft. Delicately flavoured products and food-stuffs can on storage be treated with aerosol without any danger of contamination, staining and disflavouring.

Aerosols are also being effectively used in commercial buildings and hospitals for disinfection and air-sterilization. (*Chem. Age*, 1948, No. 1511).

Chemical Industry in U. S. A.

Basic chemicals and allied industries have made such rapid strides during the last 25 years that these now represent "the largest segment in the nation's total manufacturing enterprise". The trend is further expected to continue. The reason behind this rapid development and progress is the progressive attitude of the management which is ever conscious of the value of research. It is estimated that above 65 million is annually spent by chemical producers on research. The availability of cheap hydro-electric power and easy access to raw materials are further contributory factors for this rapid development. Statistical reports available from International Trade Section of the U. S. Department of Commerce reveal that foreign sale of chemicals by U. S. A. in 1947 totalled over 800 million dollars.

(*Chem. Age*, 1948, No. 1510).

Polyisobutylene

At the high polymer forum, arranged under the auspices of the 113th Technical Session of the American Chemical Society at Chicago, a paper describing the various uses of polyisobutylene was presented. It was reported that this single chemical can be used in the preparation of face-cream, machine grease, rubber and

paint. The monomer *isobutylene*, derived from petroleum refinery gases, polymerises very rapidly at 80° and the formation of poly*isobutylene*, comprising over 1000 molecules of *isobutylene*, is complete in 5 minutes. The polymerised product varies in consistency ranging from sticky grease to a rubbery solid and can be converted into hard plastics and paints by chemical modification. The most important current use of this polymer is in Butyl Rubber which possesses the holding of air better than natural rubber. (*Chem. Eng. News*, 1948, No. 19).

Salt Industry in Ceylon

Salt is a chief source of revenue for the Government of Ceylon. Since 1945, various schemes to increase the production of salt in the island have been worked up. Solar evaporation of brine in enclosures of clay is mainly the process employed. Attempts have been made to improve the quality of salt by introducing new technique, namely, use of concrete tanks, graining pans and vacuum evaporation. By-products like gypsum, magnesium and potash salts are also collected from the salterns. A large project has recently been drawn up for the production of the island's annual needs of 50,000 tons of potash salts, 15 million tons of common salt, 100,000 tons each of gypsum and magnesia and varying amounts boric acid and secondary chemicals.

Bamag-Sarog Express Hydrogenator

This new oil hydrogenation unit, devised by Bamag Ltd., is capable of hardening fatty oils and acids at a very rapid rate. The novel feature of the plant is a special type of centrifugal pump which ensures an intensive mixing of oil, hydrogen and catalyst. The oil, preheated by outgoing hardened oil, collects in the pump-feed vessel where the catalyst is added. The mixture enters the pump wherein fresh hydrogen is injected. Arrangement is also provided for sucking into the pump chamber any surplus hydrogen collecting in the top of the feed vessel. Groundnut oil can be hardened to a m. p. of 36-38° in about 15 minutes; oleic acid can be transformed into stearic acid in 60-70 minutes and highly unsaturated oils (Sardine or Herring) can be brought down to Iodine value of 1, within approximately 60 minutes in this improved unit. (*Chem. Age*, 1948, No 1509).

Down-Jet Furnance

The B. C. U. R. A. Quarterly Gazette (No. 1) describes the principle of down-jet combustion developed by the Association. Some of the drawbacks of the orthodox combustion methods have been eliminated in the present system. No fire-bars to support the fuel nor any secondary air with the necessarily large combustion space are needed in this furnace. The coal is carried on a solid hearth provided with a clinker removal device, placed remote from the supply of air. The air for combustion is fed through

adjustable nozzles located above the fuel bed. The combustion is smokeless. No attention for ash removal is required up to 10 hours of operation but a mechanical ash removal gear is installed where continuous working is desired. The fuel falls out from a hopper under a feed edge to form a free surface at the angle of repose—the burning surface. The ash flows down and collects at the bottom. The fuel bed is thus self-cleaning and a low ash fusion point is no disadvantage. Coal to be used must be coking. For smaller types, consuming less than 2000 lbs./hour of fuel, the use of coke is recommended.

A New Metal Discovery

According to a Reuter's message, a new metal combining the properties of aluminium and steel has been discovered by Dupont Co. of Delaware from titanium ore. The new metal is silver white in colour, feels like silk after polish. It is about half the weight of steel and less than twice the weight of aluminium. It is as strong as stainless steel and possesses corrosion resistant properties like this latter and can withstand a great heat.

Hildebrand Prize for 1948

Nathan L. Drake, Chairman of Chemistry, University of Maryland, is the recipient of 1948 Hildebrand prize for his outstanding work on antimalarials. Among some eighty compounds prepared by Dr. Drake and his group at Maryland, two (a) SN 7618 or

Chloroquine, [7-Chloro-4-(4 di-ethyl-amino-1-methylbutylamino) quinoline] and (b) SN 12,276 or Pentaquine, [8-(5 -isopropylaminoamylamino) -6-methoxyquinoline, are the most successful.

Pharmaceutical Research

During 1947, the drug industry in United States of America spent at least 50 million dollars for scientific research of which the pharmaceutical manufacturers expended approximately 23 million dollars.

The researches have been carried out mostly on Sulfonamides, Antibiotics, Vitamins, endocrine preparations like insulin.

A New Vitamin

Rickes and co-workers appear to have isolated from liver an active principle, useful in pernicious anaemia, in crystalline form and they have named it Vitamin B₁₂ (*Science*, 1948, 107, 396).

Lester Smith obtained two red pigments both being highly active in pernicious anaemia—one being obtained from proteolysed liver extract and other from a non-proteolysed extract. Neither pigment were obtained in pure form but nevertheless, one obtained from proteolysed liver gave a full clinical response to a single dose of 0.3 mg. (*Nature*, 1948, 161, 638).

A New Antibiotic

One of the most interesting new antibiotics having activity against pathogenic organisms is chloromycetin, isolated from the culture of a species of *Streptomyces* which originally was found in Venezuela. It contains non-ionic chlorine and nitrogen. It possesses a considerable effect against several rickettsial agents including scrub typhus in mice and chicken embryos.

New Antimalarial Alkaloids

The new alkaloids have been isolated from the plant *Dichroa febrifuga*; one of these has been found to possess an antimalarial activity in ducks against *P. lophurae* 100 times more potent than quinine. The second compound has little activity but upon heating it is converted into the active agent. Elucidation of the structure of these compounds will be awaited with interest.

Activities of the Indian Lac Research Institute

The Annual Report of work at the Indian Lac Research Institute, Namkum, for the year 1946-47 reveals a wealth of information regarding the manufacture and uses of lac in various arts and industries.

Owing to multifarious uses of lac, e.g., in electrical insulating materials, plastic moulded goods, quick-drying paints, adhesives, rubber goods manufacture, etc., there has been an abnormal increase both in the production and export of seedlac and shellac.

Scientific investigations held at the Institute during the year under review can be broadly classified into two sections: (1) Entomological Section and (2) Chemical Section.

Under the Entomological section investigations are being conducted on biological control and on insect enemies of lac. Of the methods tested for control of insect enemies of lac, that by cold water immersion has been found to be the best both from a practical and economic points of view.

The research programme in the Chemical Section is being directed with greater emphasis on fundamental aspects of chemistry of lac. The previous work on Lac-urea-formaldehyde moulding powder has been further extended. Lac-dimethylol urea moulding compositions have been tried and it has been found that this composition yields a moulding powder possessing good impact strength and also satisfactory flow and finish. The problem of finding suitable fillers for moulding powder has been studied and it is observed that a modified Jute-stick dust will serve the purpose well. The use of lac in the manufacture of varnish and oil-cloth has been studied in details. Air-drying "oil-cloth" composition has been prepared using lac, linseed oil, lead oxide and other compositions. Fundamental researches on the chemical composition of hard lac resin has been taken up since the beginning of 1947.

Of the other investigations under this section mention may be made of researches on (i) hydrogenation of shellac and shellac compounds, (ii) effect of infra-red heat on lac and lac

film; (iii) on heat polymerisation of lac and (iv) physico-chemical studies such as, osmotic pressure of shellac solution, depolarisation of scattered light by shellac solution and di-electric properties of lac varnishes, ester gum, hydrolysed lac and lac-laminated boards and (v) shellac wax.

Immunity Bulletin

The third issue of the annual publication (published by Dr. T. N. Ghosh and Dr. A. N. Bose, Joint Secretaries, Immunity Scientific Association, Bengal Immunity Research Institute, 39, Lower Circular Road, Calcutta 16.) contain synopsis of researches carried out at the Bengal Immunity Research Laboratory 1946-47. The total number of papers published

was 43, of which 24 have been classified under "Chemical Research", 6 under "Biochemical Research", 4 under "Biological Research" and 9 under "Pharmacological Research". The subjects of research include, among others, the proteins from groundnut and sesame seeds and their utilisation, preparation of activated charcoal, studies on the starch-iodine complex, the chemistry and chemotherapy of antimalarials and of organo-arsenic and antimony compounds, the pharmacopoeial standards of protein hydrolysate, activated charcoal and Indian agar agar, the stability of vitamin A, preparation of desoxycholic acid and bating agents, studies on 'Cholera red' reaction, bacterio-static activity of sulphonamides and of *Allium sativum* and the activity of sulphonamide derivatives against streptococcal and pneumococcal infections in mice.

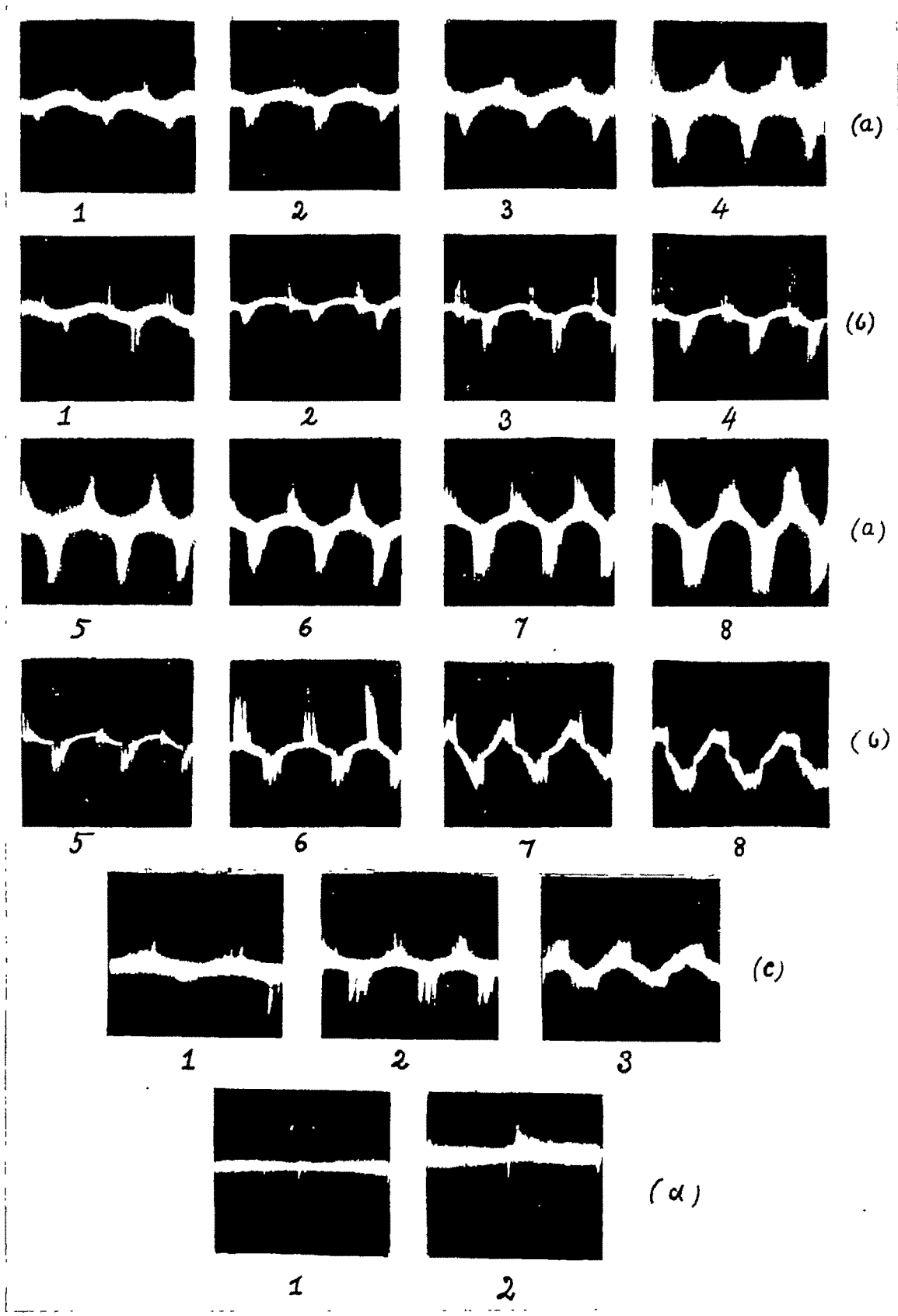


PLATE I *Oscillographic pictures of discharge current.*

1-8 in series (a) for pressure 34-1 cm.

1-8 in series (b) for pressure 34-1 cm. with the h.f. by-passed.

THE OZONIZER AND THE "LIGHT EFFECT"

BY S. DEB AND (MISS) N. GHOSH

The paper first reviews the present state of our knowledge of the so-called "Light Effect" consisting of a sharp decrease of the discharge current in an ozonizer tube on exposure to light. Results of studies made by different workers on the different aspects of the effect, e.g. its dependance on the nature of the gas used, on the intensity and frequency of incident radiation, on the variation of the applied voltage on temperature, on the manner of illumination and on the surface condition of the walls of the discharge space, are collected and systematised. It is shown that for a proper understanding of the effect it is essential that the mechanism of the discharge in the ozonizer be first understood. For this purpose oscillographic records of the discharge current have been made under different conditions; these are reproduced in the paper. The theory of the effect as originally suggested by Mitra and later developed by the authors is discussed in detail. According to this theory the origin of the effect is to be traced to the action of light on the surface charges (produced under discharge) on the walls of the annular discharge space of the ozonizer tube. Mechanism of the discharge as also that of the formation of surface charge are explained.

The theories proposed by other workers are also reviewed.

Production of ozone by the so-called silent electric discharge has been known for a long time and Siemen's ozonizer, a familiar apparatus in chemical laboratories, was introduced as early as 1858. Though so well known and so widely used for preparation of ozone, the nature of the electrical discharge passing in the ozonizer is by no means simple and has been the subject of many investigations. Unfortunately, the ordinary or even the advanced text-books on chemistry seldom explain the mechanism of the discharge and the average student is left with a vague idea about its role and nature. In recent years the study of the ozonizer discharge has come into prominence in this country because of a curious effect, generally called "A New Light Effect" first noticed by Joshi (*B. H. U. Jour.*, 1943, 8, 99, *Proc. Indian Sci. Cong.*, 1943, Part II, 74-77). Briefly the effect is as follows:

If the ozonizer, when in action, is flooded with light (visible light including red) the current passing through it is found to decrease markedly. Under optimum condition (using chlorine gas instead of oxygen and at a pressure of a few tens of mm.) the decrease of current might be as much as 94% (Joshi and Deo, *Nature*, 1944, 163, 434).

The effect seems strange because apparently the action of light, if any, would be to increase the current by promoting ionization. (It should be noted that under special circumstances a "positive" light effect *i.e.*, an increase of discharge current on illumination with light may also be obtained. See Sec. 2). Joshi and his co-workers have studied the various aspects of this effect and have published a large number of notes on the subject. Unfortunately, most of these are only in the form of very short Abstracts in the Proceedings of the Indian Science Congress Association. The purpose of the present paper is firstly, to make a review of the present state of our knowledge regarding the nature of the discharge, secondly, to give a connected account of the experimental

work on the "Light Effect" done so far and thirdly, to make a critical review of the explanations of the "Light Effect" which have been given. The theory of the effect as developed by the authors (*Science & Culture*, 1946-47, **12**, 17) of this paper from a suggestion of Prof. S. K. Mitra is also discussed in fuller detail. It is hoped that the paper would give a complete picture of the action of the ozonizer and of the light effect and would thus be of help to the future investigators in the field.

1. EXPERIMENTS WITH OZONIZER: THE MECHANISM OF THE DISCHARGE

Fig. 1(a) shows the experimental arrangement for exciting the ozonizer tube. The

FIG. 1(a)

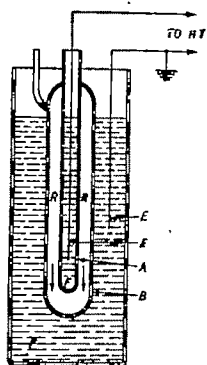


FIG. 1(b)

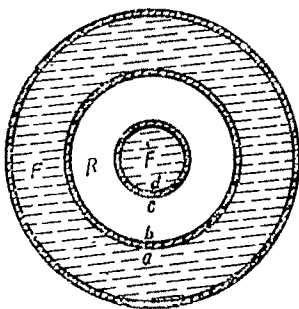


FIG. 2

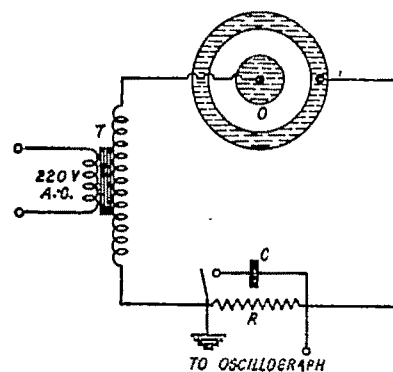


Fig. 1(a). The ozonizer tube The high tension a. c. flows through the condenser system shown in Fig. 1(b). A and B are the two concentric glass electrode surfaces; FF, the conducting liquid; platinum electrodes EE serve as the leads for the applied voltage; RR is the discharge space.

Fig. 1(b) Illustrating the condenser system in the ozonizer tube FF is the conducting liquid plates of the condensers. The dielectric is partly glass (ab, cd) and partly the gas in annular space R.

Fig. 2. Recording of the discharge current by cathode ray oscillograph The voltage developed across the resistance R is led to the oscillograph. The condenser C can be placed across R if desired to by-pass high frequency component of the discharge current.

tube is of the Brodie type and consists essentially of a double-walled glass tube through which the gas to be subjected to silent discharge flows [Fig. 1(b)]. The inner tube, as also the outer containing vessel, contain some conducting liquid (e.g. salt solution). The two conductors are connected to the output of a high voltage transformer (20,000 volts) capable of yielding a current of several milliamperes. It may be mentioned that the ozonizer as introduced by Siemen's and also of common use even now employs tin foils instead of electrolyte solution for electrical contacts.

It is obvious that the ozonizer is in effect a cylindrical condenser as depicted in Fig. 1(b) of which the conducting elements are the electrolytes in the inner and outer cylinders and the dielectric in between is partly glass (ab and cd) and partly air R or the gas which is being used. From the very nature of the apparatus it is clear that it will work only with alternating voltage, because it is then and then only that a dis-

placement current can continually flow through the system and produce continuous electrical effect.

As mentioned in the above, the nature of the discharge passing through the ozonizer is by no means simple. Warburg (*Verhand. Deut. Phys. Ges.*, 1903, p. 382) appears to be the first to have recognised this. He and his co-workers made extensive studies both of the physical mechanism of the ozonizer discharge and also of the nature of the chemical reactions proceeding with it. He pictured the action as follows. Assume, for simplicity, that the applied voltage instead of being sinusoidal is alternating between two sharp pulses of values $+E$ and $-E$ volt. If E (say $+E$) is sufficiently large, the insulation of the gas contained in the annular space breaks down and large numbers of positive and negative ions are formed. These are urged towards the two inner electrode surfaces and form surface charges. This gives rise to a field opposed to the externally applied voltage. When this field attains a particular value M , the external field, so far as the discharge is concerned, is neutralised and the discharge stops. Now if the external voltage is switched over to $-E$, the phenomenon is repeated in the opposite direction.

Warburg was, however, careful to point out that the above simple picture is not applicable in the case of an ozone tube operated with alternating voltage, because in that case the external voltage and the opposing voltage set up by the surface charges increase simultaneously making the problem more complicated. St. Sach (*Ann. Physik*, 1915, **47**, 886), however, performed experiments with A. C. and showed that the above picture of Warburg provides a useful approach to the actual mechanism of the discharge with A. C. operating voltage.

Very early in course of his investigations Warburg (*Z. tech. Physik*, 1924, 165) discovered that the discharge current had a component, the frequency of which was very high compared to that of the applied alternating voltage. Warburg and Leithauser (*Ann. Physik*, 1903, **28**, 1) measured the discharge current both by electrometer and by thermo-junction and observed that the thermo-junction always indicated a stronger current than the electrometer. They traced the origin of this discrepancy to the existence in the discharge current of high frequency components. When the electrometer was used for measurement the high frequency component was largely by-passed through the electrometer capacity as also through the self capacity of the resistance which had been inserted in the circuit for measurement of the voltage. It was, however, observed, that these high frequency currents did not contribute to the ozone formation because the rate of formation remained unaltered even when these high frequency currents were damped out by increasing the value of the resistances in the circuit. Warburg also determined the proportion of the high frequency components, using different resistances, and different amplitudes and frequencies of the applied voltage and with decreasing value of the thickness of the discharge space. The frequency component was found to be 10^5 – 10^6 cycles/sec.

Warburg, however, did not clearly explain the mechanism of the production of the h.f. currents. This was done by Klemenc, Hintenberger and Höffer (*Z. Electrochem.*, 1937, **43**, 708) who pointed out that the h.f. currents consist of a great many closely

packed unidirectional pulses rather than h.f. oscillations as originally thought of. These authors investigated the nature of the discharge current with the help of a cathode ray oscillograph (Fig. 2). The discharge current was made to flow through the resistance R and the voltage developed across it was applied to the deflecting plates of the cathode ray oscillograph. The trace on the oscillograph thus depicted the variation of current in the discharge circuit. It was observed that between the current and the applied voltage there was a phase difference of about $\pi/2$. The h.f. phenomena occurred about the points where the current trace on the oscillograph was a maximum that is, when voltage was at its zero value. The authors explained the discharge phenomenon as follows :

The applied A.C. voltage in course of its periodic cycle becomes large enough to produce ionization in the gas. The electrons and the positive ions, thus produced, move in opposite directions under the action of the external field and are deposited as surface charges on the opposite glass walls. These surface charges produce an opposing field in the discharge space so that the resultant field decreases steadily in intensity until it attains a value M at which the ionization and along with it the discharge stops. Now in course of time, as the applied A.C. voltage changes over to the opposite cycle, the external field is removed. The two oppositely charged layers are now free to neutralise themselves. But as the surface charges are on insulating (glass) surface, the neutralisation does not take place in one single spark but in a number of sparks between small isolated elements of surface charges. These sparks constitute the observed high frequency currents superposed on the main current. A study of the oscillograph trace also shows that the high frequency currents are obtained when the applied voltage passes through its zero value.

To test the above hypothesis Klemenc *et al* subjected the ozonizer to high D.C. voltage. No luminous discharge was observed even when the voltage was increased up to 15 Kv. On removing the voltage, however, and at the same time short circuiting the terminals, the whole of the discharge space showed luminous discharge. The explanation, as already stated, is as follows : The high applied field causes ionization in the annular space. The ions produced move in the discharge space and are deposited as surface charges. These layers of charges of opposite sign largely neutralise the applied field in the annular space. On short circuiting the electrodes the surface charges become free to neutralise themselves by sparks in the annular space and produce the observed luminosity.

2. EXPERIMENTAL STUDIES ON THE "LIGHT EFFECT"

As mentioned earlier Joshi has noticed that the discharge current decreases markedly when the ozonizer is exposed to light. A survey of the results of experimental studies on the effect made so far is made below.

Note : A convenient way of expressing the relative magnitude of the effect is to note the percentage of variation. Thus if $|\Delta i|$ be the change in current value (irrespective of sign) and i the original current, then $\frac{|\Delta i|}{i} \times 100$ gives the percentage value of the effect.

Table I gives a typical set of "light effect" measurement.

TABLE I

Gas used.	Exciting voltage (kV).	Pressure (in mm. of Hg).	Radiation.	% Δi .	Observer.
Cl ₂	11.2	596	White light (200 watt lamp).	35	Joshi & Deo (<i>Nature</i> , 1944, 163, 434)
Air	10	8	White light (100 watt lamp).	3.54	Tawde & Gopalkrishnan (unpublished paper)
O ₂	10	130	White light (200 watt lamp).	12	Deb & Ghosh (unpublished data)
Cl ₂	10.7	460	X-rays	17	Joshi (<i>Curr. Sci.</i> , 1944, 13, 278).
Cl ₂	"	"	White light (200 watt lamp).	25	"

(a) *Effect of the Gas used.*—It has been observed that the effect is most marked in chlorine. Under optimum condition it may be as much as 94%. Next in order come bromine, iodine, oxygen, air, nitrogen and hydrogen (Deshmukh, *J. Indian Chem. Soc.*, 1947, 24, 211; Joshi, *B. H. U. Jour.*, 1943, 8, 99; *Proc. Indian Sci. Cong.*, 1943, Part II, 74-77. According to earlier observations by Joshi (*loc. cit. B. H. U. Jour.*, 1943) the effect is not detectible and perhaps absent in monatomic metallic vapours like that of sodium. In a later communication, however, the effect is reported to have been obtained in alkali metals and in mercury using more sensitive detectors and under some special conditions (*Curr. Sci.*, 1947, 16, 19). For example, a 30% effect was obtained in potassium vapour, near the threshold potential V_m below which the gas in the discharge space is not ionized. The effect has also been observed in a number of compound gases, e.g. SO₂, HCl, NO₂ (*Proc. Indian Sci. Cong.*, 1942, Part III, *Chem. Sec.*, Abs. No. 57 and 62).

According to Joshi (*Curr. Sci.*, 1947, 16, 19) the magnitude of the effect varies in the same order as the electron affinities of the gases.

(b) *Effect of Change of Pressure.*—Starting from atmospheric pressure and gradually decreasing the same the effect first appears at a particular pressure. It then reaches a maximum value at a particular value of the pressure and then diminishes on further reduction of pressure and ultimately vanishes at about a mm or so. The maximum effect ordinarily occurs at about the middle range of pressures. With chlorine Joshi obtained the optimum effect at 46.5 cm. of pressure (*Nature*, 1944, 163, 434). The optimum pressure, however, varies with the applied voltage and with the geometry of the tube. The authors of the present note obtained the same with oxygen at about 15 cm. of pressure at 10 Kv.

(c) *Effect of the Applied Voltage and Change of Frequency.*—It has been found that the effect does not appear below the striking potential V_m of the gas. V_m is also called by Joshi (*Curr. Sci.*, 1946, 15, 281) as the threshold potential. On increasing the voltage beyond V_m both the discharge current and (Δi) increase. The percentage value of the effect, however, does not continue to increase (Joshi and Deo, *Curr. Sci.*, 1943, 12, 306). It first increases, reaches a maximum value at a voltage slightly in

excess of V_m and then diminishes with further increase of voltage. It has also been found that the proportion of the h. f. current in the discharge (which is the component of the discharge current affected by light) diminishes as the applied voltage is increased (Warburg *Z. tech. Physik*, 1924, 165; Joshi, *Proc. Ind. Acad. Sci.*, 1945, **22 A**, 389; Prasad and Jain, *ibid.*, 1947, **28 A**, 515).

The effect also varies when the frequency of the applied voltage is altered (Tewari, *Proc. Indian Sci. Cong.* 1946, Part III, *Phys. Sec.*, Abs. No. 34). Unfortunately there has not been sufficient observations in this connection. From the limited data available, it appears that the effect decreases with increase in frequency and ultimately vanishes at radio frequencies (Tewari and Prasad, *Curr. Sci.*, 1945, **14**, 229; Das-Gupta, *Science & Culture*, 1946, **11**, 318). Studies with the latter frequencies, however, is only for very small voltages at which there was no appreciable discharge. Joshi and Lad (*Proc. Ind. Acad. Sci.*, 1946, **22 A**, 293) for instance, obtained a 18% effect at 50 cycles and a 12% effect with 500 cycles in chlorine. 17 kV was used. No effect was observed with 0.94 volt at 5-10 mc/s.

Joshi (*Proc. Ind. Acad. Sci.*, 1945, **22 A**, 389) observed an appreciable effect with uni-directional pulsating voltage, i. e., rectified unsmoothed A.C. voltage.

(d) *Effect of Change of Wave-length of the Incident Radiation.*—The effect has been studied with wavelengths ranging from that of ordinary red light to that of the X-rays. (Joshi and Deo, *Curr. Sci.*, 1943, **12**, 306; Joshi, *ibid.* 1944, **13**, 278). In the ultraviolet (Joshi, *ibid.*, 1945, **14**, 317) and the visible range the effect generally increases with the lowering of the wavelength of the exciting light. Tawde and Gopalkrishnan (unpublished paper) obtained a linear variation of the percentage value of the effect within the range 536.7\AA - 5350.1\AA . A threshold value of the wave length at 8021\AA was obtained therefrom by extrapolation.

With X-rays a lower value (17%, the corresponding value for white light being 25%) was obtained (Joshi, *Curr. Sci.*, 1944, **13**, 278). However, the two values cannot be compared as nothing is definitely stated about the relative intensities of X-rays and white light. On continuous exposure for half an hour, the decrease became permanent, i. e., the discharge current did not regain its original value when the X-ray tube was switched off. No such permanent effect has been obtained with ordinary light in spite of exposure of several hours for days together.

(e) *Effect of Varying the Intensity of the Incident Light.*—Studies with chlorine, iodine and oxygen have shown that the effect depends markedly on the intensity of the incident beam, the variations being more pronounced at lower values of the intensity (Joshi, *Curr. Sci.*, 1945, **14**, 35). The result has been confirmed quantitatively by Tawde and Gopalkrishnan (unpublished paper) for a number of wave-lengths and at different pressures. From a study of the nature of the curves obtained these authors proposed the following relation for the variation of $\% \Delta i$ with the frequency and the intensity of the incident beam:

$$\% \Delta i = A I^{0.4} (\nu - \nu_0)$$

where A = a constant depending on pressure, nature of the surface of the ozonizer and applied voltage.

ν = wave number of the light used.

ν_0 = threshold frequency (in wave number) below which no effect is obtained.

I = intensity of the incident light in lumens.

(f) *Effect of Ageing.*—It has been observed that the production of light effect requires some amount of ageing of the discharge vessel (Goyal, *J. Indian Chem. Soc.*, 1947, **24**, 203). Thus Mohanty and Kamath (*Proc. Indian Sci. Cong.*, 1947, Part III, *Phys. Sec.*, Abs. No. 15) studying with oxygen have observed that the effect is small in a freshly made ozonizer and reaches a constant maximum only after sometime. The authors of the present paper have also observed a similar effect in chlorine and oxygen. It appears that the positive light effect [Sec. 2 (j)] is also affected by ageing, though the results obtained are not yet very clear. Thus Sarma (*Proc. Indian Sci. Cong.*, 1947, Part III, *Phys. Sec.*, Abs. No. 20) reports that the positive effect in iodine obtained by working at low voltage diminishes on prolonged ageing under discharge. But, according to Ranga Raja Rao (*ibid.*, 1947, Part III, *Phys. Sec.*, Abs. No. 18) a reverse effect is obtained in iodine when the wall is coated with KI and I_2 in acetone. Again according to Joshi and Bhatt (*ibid.*, 1942, Part III, *Chem. Sec.* Abs. No. 69) there are three stages $A \rightarrow B \rightarrow C$ in the variation of discharge current with time in iodine vapour. A shows discontinuities; during B the current fluctuates rapidly and the conductivity increases; in C the ageing effect is minimum. The transition from A to C depends upon temperature.

(g) *Effect of the Mode of Illumination.*—The light effect depends markedly on the manner in which the discharge tube is illuminated. The effect is found to be definitely higher if the ozonizer tube is illuminated from a side than when axially (Prasad, *ibid.*, 1947, Part III, *Phys. Sec.*, Abs. No. 17). As a matter of fact, it has been reported that with strictly axial illumination the effect is almost absent (Tawde and Gopalkrishnan, unpublished paper). These results are in accordance with the theory that the light effect is a surface phenomenon and does not depend on the volume of the gas brought under the influence of light. For instance, by covering up portions of the discharge tube by means of black paper and also by varying the inclination of the discharge tube to horizontal plane it is found that the effect is directly proportional to the effective area of the electrodes exposed to light.

(h) *Effect of Temperature Variation.*—It is possible that the light effect is affected by a change in the temperature of the discharge tube. The results obtained so far are, however, inconclusive. For instance, Joshi and Kuppuswamy (*ibid.*, 1941, Part III, *Chem. Sec.*, Abs. No. 35) report that the light effect increases with decrease of temperature in the range 7° – 75° . But Joshi and Deshmukh (*ibid.*, 1942, Part III, *Phys. Sec.*, Abs. No. 38) report an opposite result. The latter result has been confirmed by Joshi and Kane (*ibid.*, 1942, Part III, *Chem. Sec.*, Abs. No. 60) in bromine and iodine.

(i) *Effect of Surface Condition.*—The discharge current, as also the percentage of light effect, is strongly modified when the annular walls of the discharge tube are coated with different substances. Results obtained so far with different wall-coatings and gases in the discharge space are shown below in a tabular form.

TABLE II

Coating material.	Gas used.	Effect.	Observer.
Mixture of KI, I ₂ and KCl	Iodine vapour	Positive effect; a marked increase of the discharge current*	Joshi and Murthy (<i>Proc. Indian Sci. Cong.</i> , 1942, <i>Chem. Sec.</i> , Ab. No. 67)
Solution of KI, I ₂ in acetone	Iodine vapour	Negative effect; which decreases with time After 30 hours' exposure positive effect was observed.	Ranga Raja Rao (<i>ibid.</i> , 1947, <i>Phys. Sec.</i> , Ab. No. 18).
Solution of I ₂ in ether and iodoform deposited on the wall by evaporation.	Chlorine and iodine.	No effect.	Do.
Solution of I ₂ in benzene	Chlorine	15% Negative effect.	Ranga Raja Rao (<i>loc. cit.</i>) <i>ibid.</i>
Solution of I ₂ in alcohol	Chlorine	27% Negative effect.	Do.
KI and alcohol	Chlorine	38% Negative effect.	Do.
Iodoform film	Iodine vapour	Negative effect increased from 28% to 30% when iodoform film was decomposed by heating.	Do.
KI with a trace of alcohol	Iodine vapour	1250% increase of current on illumination at low voltage. When the voltage was increased a transition to normal negative effect was obtained.	Sarma (<i>ibid.</i> , 1947, <i>Phys. Sec.</i> Ab. No. 20).
Coatings of stable alkali chlorides		Current increases but corresponding light effect diminishes.	Cherian (<i>ibid.</i> , 1945, <i>Phys. Sec.</i> , Ab. No. 17).

(j) *Positive Light Effect.*—Under certain experimental conditions the discharge current shows an increase on illumination. The phenomenon is much less general than the negative effect. From observations made on many gases it has been found that the positive effect is generally obtained when the pressure in the discharge tube is comparatively high and the applied voltage comparatively low. The gases studied and the conditions under which a positive light effect has been found is shown in a tabular form below.

TABLE III

Gas used.	Pressure (in mm of Hg).	Exciting voltage.	Observer.
Air	Higher than 16.2	—	Joshi and Rao (<i>Proc. Indian Sci. Cong.</i> , 1942, <i>Chem. Sec.</i> , Ab. No. 55).
Oxygen	Higher than 22	300–3000 volts (r. m. s.)	Joshi and Cherian, (<i>ibid.</i> Ab. No. 56).
Iodine	—	150–820 volts	Joshi and Bhatt, (<i>ibid.</i> , Ab. No. 61).
Bromine	50	—	Joshi and Raghavan (<i>ibid.</i> , Ab. No. 65).
Chlorine	—	—	Do.

Conditions under which a positive light effect is obtained when the walls are coated with different materials are shown in Table II.

(k) *Other Characteristics of the Effect.*—It has been observed that the time lag, if any, between the instant of illumination and the diminution of the current is extremely small (Joshi, *Curr. Sci.*, 1944, **18**, 253). The current also ordinarily regains its original value as soon as the light is cut off. The case of X-rays is perhaps an exception to this.

The effect is not potential reversible, i. e., under otherwise identical conditions the effect at a particular voltage is found to depend somewhat on whether the value is established from a higher or from a lower voltage (Joshi and Murthy, *Proc. Indian Sci. Cong.*, 1942, Part III *Chem. Sec.*, Abs. No. 67; Joshi and Raghavan, *ibid.*, Abs. No. 64).

If the pressure is gradually decreased keeping the exciting voltage constant, it is found that at the breakdown point the discharge current is markedly unsteady. If now the tube is exposed to light, the discharge becomes steady. The steadying effect is also perceptible at much lower value of pressure though the current strength is greatly reduced at the same time.

(l) *A Note on the Effect of using different kinds of Indicating Instruments.*—Since the discharge current contains a h. f. component, it is evident that the intensity of the detected current would depend on the type of the indicator employed. It may be recalled that the indicating instrument for recording the voltage is generally placed across a high resistance R (Fig. 2) put in series with the discharge circuit. The indicating instrument used may be electrometer, valve voltmeter, metal rectifier, etc. Thermo-junction in series with the discharge circuit may also be used to measure the discharge current directly. Now, since the discharge current has a h. f. component, it is obvious that the current value as obtained from the instrument will be less if the indicating instrument has appreciable self-capacity through which the h. f. is by-passed. Warburg (*Z. tech. Physik*, 1948, 165) in his original experiment noticed the difference between the readings of an electrometer and a thermo-junction and hence concluded that there was a h. f. component of the discharge current. In recent years unfortunately this simple fact has not been recognised and there has been much confusion in the interpretation of the experimental results. Joshi and his collaborators have in fact experimented with different types of indicators, e. g. vacuo-junctions, valve voltmeters (using diodes, triodes and pentodes) and metal oxide type of rectifiers with the object of determining the effect of the different types of rectifiers and indicators on the light effect. The results obtained by these workers can all be explained if the capacities, inherent or stray, of the indicating instrument and the associated apparatus are taken into account. For instance, it is reported that thermo-junctions indicate a higher discharge current as also higher percentage Δi , while the metal oxide rectifiers show a smaller effect. The result is as expected. The metal oxide rectifiers have much larger associated capacity than the thermo-junctions which by-pass a large proportion of the h. f. current. Again, it has been found that other conditions remaining the same, the light effect obtained by using 6H6 valve, triode and pentode as detectors, were 47%, 80% and 97% respectively. Here also the input capacities of the three thermionic tubes decrease in the order mentioned. It has also been observed that if the resistance is replaced by an inductance and

the indicating instrument, e. g. valve voltmeter, is inductively coupled to it a much higher value of the percentage effect is obtained. This also is easily explained, because in this case there is much less chance of h. f. leakage.

It is of course obvious that the applied voltage at which the maximum effect appears should not be affected by the indicator used, the effect of the h. f. leakage is only to make the apparatus less sensitive. This, in fact, is what has been observed.

Joshi (*Proc. Indi. Acad. Sci.*, 1945, **22A**, 225) and also Prasad and Jain (*ibid.*, 1947, **25A**, 515) used another method of detecting the h. f. component in which they noticed a large percentage effect. In this method the h. f. part of the discharge current is picked up by a loop aerial and is measured by means of a suitable meter, a thermo-junction for instance (Fig 3). The higher percentage effect obtained is, as expected, because the aerial picked up mainly the h. f. components of discharge current which is the chief seat of origin of the effect (Narayanswami, *Proc. Indian Sci. Cong.*, 1946, Part III, *Phys. Sec.*, Abs. No. 28; Das Gupta, *ibid.*, Abs. No. 31).

FIG. 3

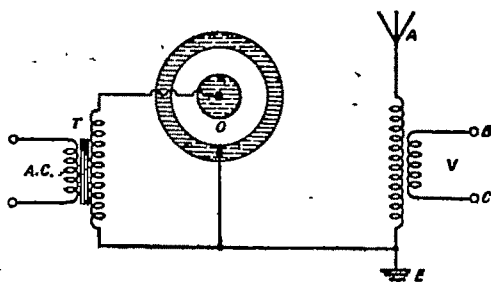


FIG. 4

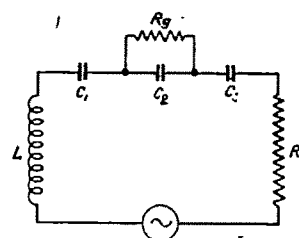


Fig. 3. Illustrating the method of studying the high frequency components by aerial pick up.

Fig. 4. Illustrating the equivalent circuit for the ozonizer discharge current. C_1 and C_3 are the capacities due to glass electrodes ab, bc; C_2 is the capacity of the gas space. R , L is the combined stray and transformer leakage inductance in the circuit; R_f is the total resistance including the losses and the resistance of Fig. 2. R_g represents the effective resistance due to the ionization in the gas space when there is discharge.

3. MECHANISM OF THE DISCHARGE : ORIGIN OF LIGHT EFFECT

We shall now discuss the origin of the light effect as originally suggested by Mitra and later developed by the authors of this paper (Deb and Ghosh, *Science & Culture* 1964-47, **12**, 17). To understand this hypothesis it is, however, essential that we first understand clearly the mechanism of the discharge phenomena in the ozonizer. This has already been broadly indicated after Warburg (*vide supra*). For understanding the details, however, it is necessary to closely examine the oscillographic records of the discharge current under different conditions. Such records have been made by us and are reproduced in Plate I.

For taking the pictures the circuit diagram shown in Fig. 2 was used. The dimensions and the characteristics of the ozonizer tube were as follows :

Radius of the inner electrode	... 1 cm.
Radius of the outer electrode	... 2 cm
Length of the tube	... 20 cm.
Voltage	... 10 kv at 50 c. p. s.
Resistance in series (R)	... 15000 ohms.

Records were taken with air at pressure 34 cm. to 1 cm. For each pressure two pictures were taken, one with a condenser C suitably placed so as to by-pass the h.f. current and the other without the condenser. Figures. 1-8 in series (a) are for different pressures without any condenser. The corresponding figures 1-8 in series (b) in the Plate are for the same pressures but with a condenser for by-passing the h.f. current.

A close scrutiny of the oscillographic pictures reveals that in general the current through the ozonizer tube has the following components.

(i) There is an approximately sinusoidal current of the same frequency as that of the applied voltage. This is clearly distinguishable as a sinusoidal trace and is particularly noticeable when the pressure is high.

(ii) Traces of current pulses shooting up (or down) from the sinusoidal trace. These current pulses can be grouped under two heads :

(a) Groups occurring during part of a half cycle in which the individual pulses are separately observable. These we call low frequency pulses. These are clearly seen in pictures in series (b) in which the h.f. component has been by-passed.

(b) Groups in which the pulses are densely packed and run into one another. These we call h.f. pulses and are seen on and around (a).

(iii) There is a set of highly damped oscillations. These are clear in pictures (1-4) for high pressure.

We further note the very interesting fact that the discharge characteristics are not the same for the two half cycles. There is a strong asymmetry which is more marked for high pressure.

(i) *Sinusoidal current.*—This is the main A. C. current through the circuit (Fig. 4) driven by the applied voltage and needs no further consideration.

(iia) *Low Frequency Pulses*—An examination of these pulses shows (remembering that the voltage across the discharge tube is a minimum at the peak of the sinusoidal trace) that their commencement marks the beginning of the discharge. This occurs obviously when the voltage V is equal to the breakdown voltage V_m . One should expect V_m to diminish as the pressure is decreased. This is what actually happens and is clearly seen in the series of pictures (1-8). For (1) the pressure is 34 cm; the striking voltage V_m is high and the point of commencement of the low frequency discharge is farthest removed from the peak of the sinusoidal trace. As the pressure is lowered the point of commencement gradually moves towards the peak, the region of the lowest voltage. The origin of these pulses is as follows :

The electrons and ions which are produced by the discharge are urged towards the electrode walls b and c respectively of the discharge tube [see Fig. 1(b)]. If these electrodes were metallic, as in ordinary discharge tube, then the electrons and ions would have delivered their charges to the electrodes and in the equilibrium state as many ions would have been produced per second as absorbed by the metal electrodes. The electrodes b and c , however, being non-conductive, produce complications. Electrons and ions produced by the discharge are urged towards the electrodes but they are unable to produce continuous current and are partly deposited as surface charges on b and c and partly remain as polarized space charge. The surface charge and the space charge together neutralise the externally applied field and the discharge stops. Which of the

two, surface charge or space charge is primarily determinative of the stoppage depends of course on their relative densities. But as the applied A. C. voltage increases in course of its cycle, the breakdown voltage is again reached overcoming the neutralising effect of the surface and the space charges. There is again ionization and again deposition of surface charge and increase of space charge; the effect of the applied external field is again neutralised and the discharge again stops. The phenomenon may thus be repeated a number of times and continue till the rate of increase of the external field becomes slower than the rate of neutralisation of the same by the increase of the surface and the space charges. This starting and stopping of discharge give rise to the low frequency pulses. The frequency of the pulses depends on several factors. Increase of mobility of the electrons and ions will quicken the deposition and thus decrease the interval between the starting and the stopping. The density of the ionization produced will also have an effect. At higher densities the rate of deposition of the charge will also increase and will shorten the interval. It will also depend upon the rate of increase of the external voltage. If the voltage rises rapidly then also the interval between the starting and the stopping of the discharge will decrease. All these factors contribute to make the spacings of the pulses different for different pressures.

A very important point to be noticed is that the surface charges are deposited not directly on the surface of the glass but rather on the adsorbed mono-molecular layer of the contained gas which is formed on the glass surface.

Formation of such a layer of the contained gas on the walls of the discharge vessel has been known for a long time. The adsorbed layer may profoundly influence the character of the discharge phenomenon. Kaplan (*Phys. Rev.*, 1932, **42**, 807) for instance has been able to produce spectra resembling those of the night sky and the aurora by specially "conditioning" the walls of the discharge tube by prolonged running. That an adsorbed layer in the ozone tube may be determinant of the light effect was also suggested by Joshi (*Curr. Sci.*, 1945, **14**, 175).

(ii) *High Frequency Pulses*.—These pulses, it will be noticed, were weaker for lower pressure but are more numerous and extended over a wider region for low pressure. The origin of these pulses is as follows:

The low frequency pulses discussed above leave the glass electrode surfaces strongly charged. When the external voltage begins to subside, the field due to these inner charges remains and if this field is strong enough, discharge takes place. But, as explained in Sec. 1, since the charges are on insulating surfaces, neutralisation proceeds in small isolated sparks in which small elements of surface charge recombine separately. These give rise to the observed h. f. pulses. When the pressure is high, the sparking potential is also high. The formation of surface charge is also rather incomplete. Neutralisation will therefore be effected in a few strong sparks producing in the discharge current a few strong pulses of extremely short duration. When the pressure is low, the sparking potential is small and also the formation of surface charge is more complete. The neutralisation in this case is brought about through a very large number of small sparks closely packed together.

To test the correctness of the above theory of the h. f. pulses pictures 1 and 2 in series (d) in the Plate were taken. In these pictures the excitation of the ozonizer was by

sharp voltage pulses, instead of by ordinary sinusoidal voltage*. In picture 1 (d) of the Plate there was no discharge and we record only the exciting pulses at right angles to the time base. In picture 2 (d) there was discharge. It will be seen that there appears now two modifications. Firstly, the exciting pulses are greatly lengthened. This is because the exciting pulses are followed by discharge and the discharge current is superimposed on them. Secondly, between the pulses there are innumerable traces of current pulses in the opposite direction. These are the h. f. pulses produced, as already explained, by the discharge of the surface charge brought about by the deposition of the electrons and ions produced by the primary pulse discharge. The fact that the h. f. current pulses are in the opposite direction is significant and is as it should be. This is because the surface charges produce voltage in the opposite direction neutralising the applied field.

A further confirmatory test for the mechanism of the discharge is furnished by pictures 1 (c), 2 (c) and 3 (c) in the Plate. These are for the case where the ozonizer had conducting (silver) coating of the inner surfaces *b* and *c*. The dimensions of the ozonizer and its other characteristics were the same as used for the series (a) and (b) of the Plate. For 1 (c) the pressure was 40 cm. For 2(c) the pressure was 20 cm. and for 3(c) the pressure was 1 cm. It will be seen that there is no dense closely spaced h. f. pulses as in pictures 1-8 in series (a). Instead, there are a comparatively few fat pulses only. This is because the surface charges being formed on conducting surfaces, the discharge of the same occurs by a few big flashes only instead of by innumerable h. f. pulses as in the case of non-conducting glass surfaces.

Asymmetry in the discharge phenomena.—The asymmetry in the different stages of the discharge is to be traced to the asymmetry of the electrode system and may be explained as follows :

For the asymmetry in the l. f. pulses which mark the main discharge due to the applied external voltage we note the following. It has been shown by Townsend (Whitehead, 'Dielectric Phenomena in Gases', 1927) that the sparking potential is different for positive and negative discharges. (Note : Discharge is said to be positive when the inner electrode is positive with respect to the outer and *vice versa*). When the pressure is high, positive discharge takes place at a voltage lower than the negative discharge. As the pressure is reduced the two sparking potential values approach each

* The pulses were obtained in the following way. Radio frequency pulses as used for ionospheric exploration were picked up and rectified by a suitable circuit. Adjustments were made so that the input coil *L* of the rectifier tube together with its stray capacities presented an anti-resonance circuit to the incoming radio frequency. The rectifier output was freed from radio frequency components by means of a combination of by-pass condenser *C* and r. f. filter and was applied across the two terminals of the ozone tube. The dimensions of the ozonizer used and its other characteristics were as follows :

Radius of the inner electrode	4 mm
Radius of the outer electrode	10 mm.
Length of the tube	15 cm.
Magnitude of the voltage pulse	2500 volts.
Circuit resistance	50,000 ohms

other and become equal for $\frac{\chi}{p} \approx 150$ (χ = applied field in volts per cm., p = pressure in mm of Hg.) With further reduction in pressure the state of affairs is reversed and negative discharge takes place for a lower voltage. The above observation of Townsend are, of course, for metallic electrodes. We may, however, assume that the remark also holds, qualitatively at least, in the case of the ozonizer in which the inner and the outer electrodes are insulators. Asymmetry in the discharge which produces the l. f. pulses is thus expected.

The asymmetry in the h. f. pulses is also a consequence of the asymmetry of the electrodes. It is easy to see that the density of the surface charge on the inner electrode will, on account of its smaller area, be higher than that on the outer electrode. Also, we recall that owing to the higher mobility of the electrons the surface charges are mostly electronic i.e. negative. It therefore follows that when the inner electrode is negative, the h. f. pulses will be stronger but since the surface area is smaller, they will be spread over a smaller part of the cycle. When the outer electrode is negative, the h. f. pulses will be less intense but on account of greater surface area will be spread over a larger part of the cycle. This is as actually observed.

An interesting consequence, which is borne out by observations, follows from the above considerations. When the pressure is high, the sparking potential is also high and the breakdown voltage may be attained only during the half cycles when the inner electrode is positive. In such case the l. f. pulses will be confined to one half-cycle only. The h. f. component, however, since it is caused by the discharge of the surface charges, will be spread over a part of the rest of the cycle. When the pressure is low there is full display of the high frequency pulses in both half cycles.

(iii) *Damped Low Frequency Oscillation*.—The frequency of these oscillations is related to the circuit constants L , C , R . (Fig. 4). They are produced in the process of recombination of the polarised space charge.

Origin of the Light Effect.—The origin of the light effect is now easily understood. When the electrode surface is irradiated there is electron emission from the surface charge and its density is considerably reduced. The density of the high frequency pulses, which are caused by sparking between the surface charges of opposite signs of the two walls of glass electrodes, is thus also considerably reduced. This causes reduction in the total current flowing through the ozonizer and produces the main characteristic of the light effect. The other prominent features of the light effect, e.g., its dependence (a) on the nature of the gas used, (b) on the frequency and the intensity of the incident radiation and (c) on the magnitude and the frequency of the applied potential are also satisfactorily explained on the above hypothesis.

To explain how the percentage effect depends on the nature of the gas used, we recall that the surface charge which controls the discharge phenomena is formed on the adsorbed layer of molecules on the glass surface. The surface charge will therefore be quickly and more completely formed if the electron affinity of the gas molecules is high. Hence, the greater the electron affinity of the gas used, the greater will be the proportion of the h.f. component (produced by the discharge of the surface charges) in the total current and the greater the percentage reduction of the total current on irradiation. That this is so is confirmed by the experimental results. It is well known that for the

series-chlorine, bromine, iodine and oxygen the readiness with which an adsorbed layer is formed, as also the electron affinity decrease progressively from chlorine to oxygen. The percentage light effect for these gases also decreases in the same order (Joshi, *B. H. U. Jour.*, 1943, 8, 99).

It is found that the percentage effect increases when the intensity and the frequency of the incident radiation are increased. That this will be so is obvious on the above hypothesis, because an increase of intensity and of the frequency of the incident radiation will cause increased reduction of the surface charge density and such reduction will be followed by a reduction in the h.f. current. It is, however, difficult to predict the exact nature of relationship with the frequency of the incident radiation due to our limited knowledge of the nature of the surface forces. It may follow different laws in different ranges of wave-length.

The decrease of the percentage effect with the increase of the applied voltage is caused by the diminution of the proportion of the h.f. current in the discharge (Warburg, *loc. cit.*, Prasad and Jain, *loc. cit.*). The origin of the latter can be understood from the following rough consideration.

As already explained, the surface charges the neutralisation of which produces the h.f. pulses are also responsible for stopping the main discharge (l.f. pulses). Now if M be the extinction voltage (*i.e.*, the net voltage across the discharge space at the critical instant when the discharge stops), then the opposing voltage, set up by the surface charges, may be put equal to $KV_o - M$. (Here V_o is the peak value of the potential and K is a constant depending on the capacity system in the ozone tube and is less than 1). The density of the surface charge is thus proportional to $KV_o - M$, while the strength of the total current is proportional to $V_o - V_m$ where V_m is the threshold value of the applied voltage at which the discharge begins. The percentage of h.f. in the discharge will therefore be proportional to

$$\frac{KV_o - M}{V_o - V_m} = f \text{ (say)}$$

therefore,

$$\frac{df}{dV_o} = \frac{M - KV_m}{(V_o - V_m)^2}$$

Now, KV_m being the value of the starting potential is greater than M , the extinction potential. Hence, the numerator is a negative quantity. df/dV_o is also therefore a negative quantity which means the ratio f which is proportional to the percentage effect would decrease with the increase of the applied voltage. The slight increase that is observed in the range of voltage slightly in excess of V_m is due to the unstable nature of the discharge in that range.

To explain the effect of frequency we note that as the frequency of the applied voltage is increased the pulsation time becomes equal to and finally less than the time required for the full deposition of the charge. Increase of frequency therefore causes a decrease in the density of the surface charge. Hence the h.f. component of the discharge as also the light effect decrease as the frequency is increased.

Other features of the light effect such as the effect of ageing, of the mode of illumination, and of surface condition are also easily explained on the basis of the proposed

hypothesis. That a freshly made ozonizer requires some time for the display of the full effect is due to the fact that the formation of adsorbed layer of gas molecules requires some time. The almost negligible light effect when the ozonizer is illuminated longitudinally is simply because in this case the electrode surfaces are ill illuminated. That the surface condition should affect the light effect is obvious. Because, as is well known, adsorption of a gas on a surface is strongly dependent on its physical and other condition such as freedom from contamination.

In fact all the above and other characteristic features of the light effect lend support to the correctness of the proposed hypothesis.

4. OTHER SUGGESTIONS ON THE ORIGIN OF THE "LIGHT EFFECT"

It would be interesting to discuss some of the suggestions made from time to time by other workers in the field to explain the origin of the light effect. This will show how futile it is to attempt any explanation without first understanding the peculiar mechanism of the discharge phenomena in an ozonizer.

1. Joshi has offered three different suggestions, not related in any way to each other, on three occasions. These are as follows :

(i) The *ad hoc* assumption is made that an increase of the threshold potential V_m on irradiation is responsible for the origin of the light effect (Joshi, *Proc. Ind. Acad. Sci.*, 1945, **22A**, 389). The explanation is based on the observed fact that the discharge current increase as $V - V_m$ increases, where V is the applied potential. No reason is, however, given why V_m should increase on irradiation (as indeed there is none). Apart from this, the observations of Warburg (*loc. cit.*) and also of Prasad and Jain, (*loc. cit.*), that the proportion of high frequency current diminishes with increase of applied voltage go against the explanation. This is because as already indicated, it is the high frequency component of the current which is affected (generally decreased) on exposure to light and is determinative of the light effect. If irradiation increases V_m , i.e., decreases $(V - V_m)$ then the proportion of high frequency current would also increase. In other words, the effect of light would be to increase the h.f. component of the discharge current. This is just the reverse of what is actually observed.

(ii) Joshi (*Proc. Indian Sci. Cong.*, 1946, Part III, *Phys. Sec.*, Abs. No. 26) also suggests that "under discharge an activated layer is formed on the electrodes and it is in dynamical equilibrium with the gas phase; as a primary step photo-emission occurs from the active layer and the photo-electrons thus emitted are captured by the highly electro-negative element present in the vessel to produce negative ions. These negative ions account for the effect. Further, they produce an opposing electro-static field which finally cuts off photo-electric emission. On shutting out incident light these electrons producing the electrostatic field return to the electrodes and thus produce an instantaneous reverse effect". (See also *Curr. Sci.*, 1945, **14**, 175). [In some later communication Joshi (*Curr. Sci.*, 1945, **14**, 317; *1947, **16**, 19), makes the further suggestion that the production of negative ions is facilitated by the fact that

* In this paper Joshi gives an expression (Equation No. 1) for the discharge current as function of the circuit constants and applied voltage. But unfortunately the expression is wholly wrong.

the molecules are excited and that according to Frank such molecules have greater electron affinities.] The explanation, as will be noticed, is at best a complicated one and invokes quite a number of steps: Formation of an "activated layer"; photo-emission from the same; formation of negative ions; production of an opposing electric field which cuts off the photo-electric emission. Perhaps, of all the steps suggested, the first, namely, the formation of an "activated layer" is the fundamental one. No reason, is however, assigned for its formation nor it is mentioned anywhere what the "activated layer" consists of—electrons or gas molecules. Further, the word "activated" has been used loosely without proper appreciation of its significance. We know of cases of activated adsorption at relatively high temperatures in which unlike the case of ordinary adsorption the binding energy of adsorbed atoms is extremely high. Thus, for instance H_2 in contact with glass shows activated adsorption at about 400° . In this case, the heat of adsorption is of the order of 30,000 calories as compared with a few hundred calories for ordinary adsorption. Binding energy for chlorine is much higher than this. For it is well known, that chlorine, bromine, etc. are adsorbable to a far greater extent than oxygen, hydrogen or nitrogen. If by "activated layer" is meant a layer formed by activated adsorption, the binding energy of the gas molecules, *i.e.*, the heat of adsorption would be of the order of 10 eV corresponding to radiation of wave-length less than 1250\AA . But the light effect is observed even with red radiation. It is difficult to see how an "activated" adsorbed layer would be disturbed by light of such colour unless of course something else is meant by "activated layer". This, however, has not been explained and has been left vague.

Joshi further argues that photo-electrons liberated by the incident light from the "activated layer" thus formed are captured by the gas molecules; hence there is a reduction in ionic mobility and a consequent reduction in the current. It is difficult to follow the reasoning. Firstly, the ionization potential of the electro-negative gas used is very high. Hence, there can be no photo-emission from a layer of molecules of such gas by the light of wave-length used. Secondly, before irradiation the discharge space contains electrons and excited molecules. According to Joshi the excited molecules will capture the electrons and reduce ionic mobility. Thus the reduction effect, if any, will already be there. The first electrons liberated by the incident light will tend to increase the current and even accepting Joshi's arguments, the capture of these electrons will at best check this tendency to increase. One fails to see why it will cause a decrease of the total current.

(iii) Joshi's *Curr. Sci.*, 1946, 16, 19) third suggestion is that the "activated layer" being formed on a dielectric surface might contain ions of both signs. "The electrostatic and inductive influence on the ions and electrons in the gas phase, modifies the annular capacity distinctive of normal gas. A photo-electric emission from the layer entails a capacitive change (and therefore a phase shift) leading to the effect".

Unfortunately, it is not explained how exactly the surface layer exerts "electrostatic and inductive influence on the ions and electrons in the gas phase" or how it "modifies the annular capacity distinctive of the normal gas" or how "the capacitive change (and therefore a phase shift)" following upon photo-electric emission should lead to the light effect. It is well known that presence of electrons and ions in an ionized gas

reduces its dielectric constant. But this reduction in the case under consideration, even granting that it may have something to do with the light effect, is negligibly small.

2. Prasad (*Nature*, 1945, **166**, 362) applies Kramer's quantum mechanical dispersion formula and imagines ionization to be an extreme case of photo-excitation and tries to show that the reduction in dielectric constant of the gas in the discharge space due to optical excitation might be responsible for the observed change in discharge current. According to the author this suggests that the effect should be confined to the dielectric part of the current.

Without going into the merits of the hypothesis, it might be mentioned that the light effect is a surface effect (Sec. 3). But according to the authors hypothesis the magnitude of the effect should depend on the volume of the excited gas. Further, experimental results of Das Gupta (*Science & Culture*, 1946, **11**, 318) and of Tewari and Prasad (*Curr. Sci.*, 1945, **14**, 229) contradict the hypothesis. These authors while experimenting with radio frequency voltage, when the current was entirely of displacement type, observed that the light effect is negligible, if not absent.

3. Sahay (*Curr. Sci.*, 1945, **14**, 122) has suggested that the effect of illumination is to produce excited atoms in the discharge space. These suffer a large number of collisions of the second type, with the electrons thereby reducing the mobility of the latter. Since the coefficient of recombination is large for slower electrons, a large number of them will disappear through recombination causing a diminution of the discharge current.

Here again, like the hypothesis of Prasad, a volume effect is presumed. Also it might be said that according to the mechanism assumed ordinary D. C. discharge tube should also show the light effect. But as already stressed the light effect is peculiar to the ozonizer tube only.

5. CONCLUDING REMARKS.

The sharp decrease in the discharge current of an ozonizer on exposure to light provides a spectacular demonstration, on the one hand, of the formation of surface charge on the glass walls of a discharge tube and on the other, of the instantaneous action of light on the same. That the so-called "light effect" is a peculiarity of the ozonizer discharge on account of the peculiar nature (insulated) and disposition of the electrodes had not been properly realised. Incidentally, it shows how vague had been our knowledge of the discharge mechanism in the ozonizer—a familiar apparatus in a chemical laboratory. The phenomenon deserves wider attention and ought to find a place in text books.

The fact that the origin of the light effect may be traced to the action of light on electronic surface charges formed on the glass electrode surface of the ozonizer was suggested to us by Prof. S. K. Mitra.

We take this opportunity to express our grateful thanks to Prof. Mitra for the suggestion and for the advice and help he gave us in the preparation of the paper.

PRODUCTION OF THE JOSHI EFFECT IN OXYGEN UNDER SILENT
ELECTRIC DISCHARGE. PART II. INFLUENCE OF INTENSITY
AND FREQUENCY OF THE INCIDENT RADIATIONS

By S. R. MOHANTY AND G. S. KAMATH

The Joshi effect Δi in oxygen has been studied at different exciting potentials V of 50 cycles frequency as a function of the light intensity I , and with different wave bands in the visible. At constant V , increase of Δi with I is first rapid; saturation sets in at large I . This has been ascribed, on Joshi's theory, to the development of an opposing electro-static field in the immediate neighbourhood of the photo-active boundary layer on the excited electrodes. The Joshi-Lakshminarayana equation, viz., $\Delta i = aI^b$ (a and b being constants) holds over a fairly wide range of moderate intensities. At higher V , the initial rise of Δi with I and the corresponding tendency to saturation are comparatively pronounced than at a lower V . The non-linear dependence of Δi on I discriminates the Joshi effect from the classical metal-in-vacuum type photo-electric phenomenon.

At a given V , Δi varies in the order: unfiltered white > blue > green-red. The selective absorption of oxygen in the visible is but feeble. It is maximum in the green-red. The Joshi effect is, however, markedly less in this than in the blue, which supports Joshi's postulate that Δi is not a consequence of selective absorption.

The oxygen, activated under the silent electric discharge, shows an appreciable Joshi effect Δi has been established by the authors in a previous communication (this *Journal*, 1948, 26, 405). The present communication reports results for the dependence of Δi on oxygen at different exciting potentials upon the intensity and the frequency of the incident radiations, in the visible.

EXPERIMENTAL

The general experimental arrangement and the procedure for observing Δi were essentially similar to those described in Part I of this series (Mohanty and Kamath, *loc. cit.*). A Siemens' type glass ozoniser filled with purified oxygen at a pressure of 27 mm. Hg (20°) was excited by transformer discharges of 50 cycles frequency in the primary. The current indicator consisted of a sensitive mirror galvanometer actuated by a Cambridge vacuo-junction. A water cell interposed between the ozoniser and the source of radiations, viz., the incandescent (glass) bulb, served to cut off the less refrangible heat rays.

The intensity of the incident radiations was varied by altering the distance d between the ozoniser and the source, in the range of 10—200 cm. The gas was excited at a constant applied V . Galvanometer deflections were noted in the dark, and under irradiation with the source at different d from the ozoniser. From these, the discharge current in dark i_d , that under irradiation i_L , the net Joshi effect $\Delta i = i_L - i_d$ and the proportionate effect $\% \Delta i = 100 \Delta i / i_d$ were calculated. The relative intensities I were computed to a

first approximation from the inverse square law. The variation of Δi with I was studied at different V in the range of 0.8—1.5 kV (r. m. s.). A typical set of observations is shown in Table I.

TABLE I

Influence of light-intensity on the Joshi effect in oxygen at different exciting potentials.

$pO_2 = 27$ mm (20°). Temp. = 27°. Frequency of A. C. supply = 50 cyc./sec.

Detector = vacuo-junction. Source of irradiation = 200 volt, 200 watt (glass) bulb

d	Intensity (relative) I	0.8 kV		0.93 kV		1.07 kV		1.2 kV		1.33 kV	
		Δi	% Δi	Δi	% Δi	Δi	% Δi	Δi	% Δi	Δi	% Δi
10 cm.	1000	6.33	44	5.66	39.1	4.59	34.8	3.86	29.5	3.93	29.3
20	250	4.5	31.6	4.34	30	3.19	24.2	2.83	21.6	2.94	21.9
30	111	3.71	25.8			2.56	19.4	2.26	17.3		
40	62.5	2.99	20.8	2.86	19.7	1.92	14.6	1.90	14.5	2.24	16.7
50	40.0	2.90	20.2			1.66	12.6	1.50	11.5	1.94	14.5
60	27.8	2.35	16.3	2.21	15.3	1.31	9.9	1.25	9.6	1.67	12.5
80	15.6	1.82	12.7	1.69	11.7	0.98	7.5	0.87	6.7	1.29	9.6
100	10.0	1.66	11.5	1.41	9.7	0.86	6.5	0.67	5.1	1.17	8.7
120	6.9	1.31	9.1	1.00	6.9	0.58	4.4	0.55	4.2	0.89	6.6
140	5.1	1.13	7.9	0.85	5.9	0.43	3.3	0.49	3.6	0.77	5.7
160	3.9	1.04	7.2	0.71	4.9	0.19	1.3	0.39	3	0.46	3.4
180	3.1	0.83	5.8	0.42	2.9	0.10	0.8	0.27	2.1	0.38	2.8
195	2.6	0.68	4.7	0.31	2.1	0.06	0.5	0.23	1.8	0.32	2.4

The effective frequency of the radiations was varied by the use of long strips of coloured glass. The familiar Watten or similar filters could not be used on account of the appreciable size of the ozoniser which was necessary to ensure a large enough i so that Δi could be observed with sufficient accuracy. The discharge current i due to different V in the range of 0.5—3 kV was observed (i) in the dark, (ii) under irradiation (7800–3700 Å) from a 200 watt (glass) bulb run at 200 volts; and with (iii) blue (5100–

4080Å), (iv) green (6060-4830Å) and (v) red (7390-6010Å) filters added to (ii). The transmission limits quoted above were observed from the corresponding spectra taken with a Hilger constant deviation spectrograph on a Kodak P/1200 super-panchromatic plate with an one minute exposure. Using the water filter, the relative total intensities observed with a Kipps' 37 thermopile were : unfiltered white (128), red (65), blue (47) and green (3). In Table II, which contains but one representative set of observations, are shown Δi and $\% \Delta i$ for different V under the above wave bands.

TABLE II

Influence of the light-frequency on the Joshi effect in oxygen at different exciting potentials.

$pO_2 = 27$ mm (20°). Temperature = 29° . Frequency of A.C. supply = 50 cyc./sec.

Detector = vacuo-junction. Source of irradiation = 200 volt, 200 watt (glass) bulb.

V in kilo-volts (r.m.s.)	Filtered Red 7390-6010 Å.		Filtered Green 6060-4830 Å.		Filtered Violet 5100-4080 Å.		Unfiltered White 7800-3700 Å.	
	Δi .	$\% \Delta i$.	Δi .	$\% \Delta i$.	Δi .	$\% \Delta i$.	Δi .	$\% \Delta i$.
0.67	0.37	2.7	0.19	1.4	2.76	19.9	4.00	28.8
0.8	0.50	3.2	0.22	1.4	2.93	19	4.14	26.8
0.93	0.33	2.2	0.16	1.1	2.31	15.4	3.38	22.5
1.07	0.24	1.6	0.07	0.5	1.90	13	2.80	19.1
1.2	0.24	1.7	0.10	0.7	1.76	12.1	2.61	18.0
1.33	0.21	1.5	0.07	0.5	1.35	9.6	2.19	15.5
1.47	0.21	1.5	0.07	0.5	1.31	9.3	2.07	14.7
1.6	0.17	1.2	0.10	0.7	1.25	8.8	1.96	13.8
1.73	0.17	1.2	0.10	0.7	1.27	8.8	2.01	13.9
1.87	0.17	1.2	0.07	0.5	1.17	8.0	1.80	12.4
2	0.18	1.2	0.07	0.5	1.00	6.8	1.60	11
2.13	0.17	1.2	0.10	0.7	1.06	7.2	1.62	11
2.27	0.17	1.1	0.11	0.7	1.03	6.8	1.58	10.5
2.4	0.19	1.2	0.13	0.9	0.81	5.3	1.40	9.2
2.53	0.10	0.6	0.07	0.4	0.75	4.7	1.34	8.5
2.67	0.06	0.4	0.03	0.2	0.74	4.7	1.18	7.5
2.8	0.09	0.6	0.03	0.2	0.60	3.7	1.03	6.4

DISCUSSION

Data in Table I show that, similar to the observations of Joshi and co-workers (Joshi, *Proc. Indian Sci. Cong.*, 1943, Part II, pp. 70-75; *J. B. H. U.*, 1943, 8, 99; Joshi and Deo, *Nature*, 1943, 161, 561; Deo, *Indian J. Phys.*, 1944, 18, 84; *Curr. Sci.*, 1944, 13, 44) in chlorine, Δi in oxygen at constant V increases with I . Further, the variation of Δi with I is more prominent at small values of I , and slows at larger I when Δi tends to a limiting value, indicative of saturation (Joshi, *Curr. Sci.*, 1945, 14, 35; 1944, 13, 278). That the variation of Δi is influenced by the initial value of I is evident from the following: At 0.8 kV, *e. g.*, whilst about a four-fold increase of I from 2.6 to 10.0 in relative units enhances Δi from 0.68 to 1.66, *i. e.*, by 2.44 times, a similar rise of I from 10.0 to 40.0 increases Δi only 1.75 times, 1.66 to 2.90. At still higher light-intensities, the rise in Δi with I is but small. Thus *e. g.*, variation of I from 250 to 1000 increases Δi from 4.54 to 6.33, *i. e.*, by 1.39 times. These findings in oxygen support Joshi's observation (*Proc. Indian Sci. Cong.*, 1943, Part II, 70-75; *J. B. H. U.*, 1943, 8, 99), based on the non-linearity of the Δi - I relationship, that this phenomenon cannot, in the first instance, be identified with a possible negative photo-electric effect.

The rate of increase of Δi with I is influenced appreciably by the exciting potential. At higher V , the initial rise in Δi is comparatively rapid; the corresponding tendency to saturation is also more pronounced. Thus, whilst at 0.8 kV, increase of I from 2.6 to 10.0, 10.0 to 40.0 and 250 to 1000 enhances Δi respectively by 2.44, 1.75 and 1.39 times the corresponding values at the lower I , at 1.33 kV the increase is respectively 3.66, 1.66 and 1.33 times.

Joshi and Lakshminarayana (*Proc. Indian Sci. Cong.*, 1945, Part III, *Phys. Sec.*, Abs. No. 12) correlate Δi and I in the form

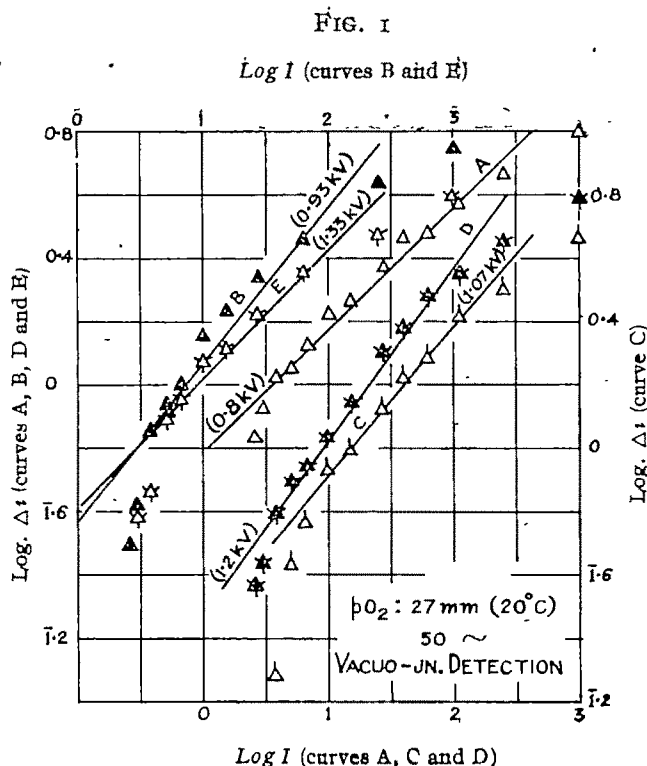
$$\Delta i = aI^b$$

where a and b are constants. This gives

$$\log \Delta i = \log a + b \log I,$$

so that the plot of $\log \Delta i$ against $\log I$ should be a straight line. The actual plots (Fig. 1) reveal that the Joshi-Lakshminarayana equation holds over a fairly wide range of moderate intensities, *e. g.*, over $I=3.9$ to 111 at 1.2 kV. It is significant that such a simple relationship should operate over about a 28 fold variation of I , despite the approximations involved in the assumption of the inverse square law for the large-size body source employed. At very high and very low intensities, however, the equation fails, and a more comprehensive one will be necessary under these conditions.

A possible explanation of the tendency to saturation of Δi at large I suggests itself from the theory of this Δi phenomenon due to Joshi (*ibid.*, 1946, Part III, *Phys. Sec.*, Abs. No. 26, 1947, Abs. No. 25; *Curr. Sci.*, 1946, 16, 281; 1947, 16, 19).



According to this, the formation on the excited electrodes of an adsorption-like ionic + molecular boundary layer is primary to Δi . Photo-electrons released from this layer are captured by the electro-negative gas particles in the discharge space to form slow moving negative ions which reduce i by a space-charge effect. The accumulation of these negative ions in the immediate neighbourhood of the photo-active layer brings into existence an opposing electro-static field which slows down the primary photo-electron emission, leading not only to the non-linear variation of Δi with respect to I , but a disproportionate inhibition to increase of Δi with I .

As is seen from Table II, Δi at constant V varies in the order : white $>$ blue $>$ red $>$ green. The relative effect $\% \Delta i$ also varies in the same order. Thus *e. g.*, at 0.67 kV, $\% \Delta i$ due to (unfiltered) white light was 28.8. This decreased to 19.9 due to the interposition of the blue filter. Substitution of the blue filter with the green and the red filters reduced markedly the magnitude of Δi ; $\% \Delta i$ was, at the above V , 1.4 and 2.7 respectively. The greater Δi under blue despite its low intensity (47), when compared with red (65), indicates, as has been observed by Joshi and co-workers (Joshi, *Proc. Indian Sci. Cong.*, 1943, Part II, 70-75; Joshi and Deò, *loc.cit.*; *Curr. Sci.* 1943, 11, 306; *Nature*, 1944, 153, 434; Deo, *Sci. & Culture*, 1943-44, 9, 253; *Proc. Ind. Acad. Sci.*, 1944, 19A, 117) in chlorine, that frequency is the more predominant factor than intensity in the production of this phenomenon. That Δi under green was slightly less than that under red might be due to I_{green} (3) being relatively far too small compared with I_{red} (65). With less disparity between I_{green} and I_{red} ,

it is likely that the *effect* in green might be greater than that in red, i. e., frequency-wise.

Oxygen absorbs in the visible, at 7594 Å (red), 6867 Å (red), between 6360 and 6225 Å (orange), 5810 and 5675 Å (yellow), at 5350 Å (green), between 4795 and 4750 Å (blue) and at 4470 Å (indigo) (Jansen, *Compt. rend.*, 1885, **101**, 11, 649; 1886, **102**, 1352; 1888 **106**, 1118; **107**, 672; Egoroff, *ibid.*, 1885, **101**, 1143; Liveing and Dewar, *Phil. Mag.*, 1888, **26**, 286; Dewar, *Chem. News*, 1893, **67**, 210; Shaver, *Proc. Roy. Soc. Canada*, 1921, **18**, 7). It would appear from this that the extent and the intensity of absorption is greater in the red-green than in the blue, which is just the reverse of the order in respect of Δi now reported. Furthermore, the above absorption is detectable only with (up to 60 metres) long tubes filled with highly compressed (up to 140 atmospheres), or with liquefied gas. As suggested by Joshi (*Proc. Indian Sci. Cong.*, 1943, Part II, 70-75) therefore, it is extremely unlikely that the *effect* Δi is entirely a consequence of selective light absorption.

Grateful thanks of the authors are due to Professor S. S. Joshi for suggesting the problem, and for his kind interest and valuable guidance.

DEPARTMENT OF CHEMISTRY,
BENARES HINDU UNIVERSITY.

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MAGNETO-CHEMICAL STUDIES IN VALENCY. PART VI. BOND-TYPE AND STEREOCHEMISTRY OF FOUR-COORDINATED COPPER COMPLEXES

BY PRIYADARANJAN RÂY AND DWIJENDRA NATH SEN

The magnetic susceptibility of a large number of copper compounds has been measured both at the room temperature and also, in a few cases, at low temperatures (-13° to -190°) for the purpose of θ -correction. From a comparison of the moment values, particularly after θ -correction, it has been shown that the 4-coordinated copper complexes can be divided into two groups: one with moment values lying between 1.72 and 1.82 Bohr and the other with values between 1.90 and 2.20 Bohr. The division, though not always a very sharp one, is still quite significant. It is, therefore, suggested that in the former the bond is homopolar of the dsp^3 planar square type and in the latter it is either ionic or covalent of the tetrahedral sp^3 or planar sp^3d type. The lower moment value of the first group results from more or less complete quenching of the orbital moment of the single unpaired electron raised to the outermost 4- p level of the atom, where it is fully exposed to the electric field of the neighbouring atoms and ions, away from the nucleus screened by the co-ordinating electrons. This difference in moment value serves to distinguish between the two types of copper complexes, the penetration and the associated ones, though, in both, the central copper atom contains one unpaired electron. It is also significant to note that all those complexes with lower moment values (1.72–1.82) are either black, brown, red, greenish yellow or violet-blue, while others with higher moment values are green, blue or blue-violet. A relationship between the colour and the bond type or structure of the complex is thereby suggested, as in the corresponding nickel complexes.

It is now well known that the determination of magnetic moment serves as a very useful means for studying the nature of the bond and the configuration of a co-ordination complex, particularly in the case of transitional elements like iron, cobalt, nickel and silver. This magneto-chemical method of study has gained special significance since the development of the quantum mechanical theory of co-ordination compounds by Pauling (*J. Amer. Chem. Soc.*, 1931, 53, 1367, 3225). For, in the case of complexes with any of the above-mentioned elements furnishing the central atom, a profound alteration in the magnetic properties of the latter is observed according as the bond involved in the formation of the complex is ionic or covalent; and according to Pauling's theory, this is closely related to the structure of the complex molecule as well. But in the case of trivalent chromium and bivalent copper no apparent difference in the magnetic properties is predicted by the theory. A consideration of the electronic structure of the simple cupric and nickelous ions, as well as of their atoms in four-coordinated complexes on the basis of this theory, makes it clear.

From the electronic configuration shown above it will be found that the theory postulates the occurrence of two types of co-ordination complexes differing in structure, viz., tetrahedral (sp^3 bonds) and planar square (dsp^3 bonds). Of these, the electronic configuration of the central atom of the tetrahedral complexes remains undisturbed as in their simple ions. Consequently, the bonds may resonate with the ionic type, and the magnetic moment of the central atom becomes undistinguishable from that of the

	Argon shell	3d	4s	4p	4d
Cu ⁺⁺	18				
Do (complex tetrahedral)	"				
Do (complex planar)	"				
"	"				
Ni ⁺⁺	"				
Do (complex tetrahedral)	"				
Do (complex planar)	"				

corresponding ion. This is amply borne out by experimental results. In the case of square nickel complexes with dsp^2 bonds, all the nickel electrons become paired, with the result that the substances become diamagnetic and are thus sharply distinguished from the simple nickel ion or its tetrahedral complexes, as these latter contain two unpaired electrons. In the case of copper, however, both the tetrahedral and planar complexes contain one unpaired electron like the simple copper ion. Hence, their magnetic properties should, on this consideration, be practically identical. In fact, all copper complexes, as well as the simple cupric ion, show a moment value of 1.73–2.20 Bohr magnetons. This approaches more or less the theoretical values of 1.73 μ_B for one unpaired electron on the basis of Heise-Stoner's formula. But on a close examination, it will be found that in the square copper complexes the unpaired electron is promoted to a higher level, 4p, whereas in the simple cupric ion and its tetrahedral complexes it occurs in the 3d-level. It is believed that this is likely to produce a slight but measurable difference in the magnetic moment between the tetrahedral and square complexes. Pauling, in fact, suggested that the moment value of the square copper complexes should be slightly lower than that of its simple ion and tetrahedral complexes, because of the greater quenching effect of the more unsymmetrical field of the attached groups in the former upon the residual orbital moment (Pauling, "The Nature of the Chemical Bond," 1940, p. 141). For the moment of the cupric ion in solution (1.95–2.20)

is always higher than the theoretical value of $1.73\mu_B$ on the basis of Bose-Stoner's formula, due to small contribution by the orbital moment. But it might also be pointed out that in the square complexes, the lone unpaired electron, being removed to a higher level and screened off by the co-ordinated electron-pairs of the attached groups, is less influenced by the nuclear field of the central atom; consequently, the perturbing and quenching effect of the field of the neighbouring atoms and ions on its orbital moment will be more in evidence. Both the above-mentioned factors might, however, be expected to make their contribution to this end. Hence, the moment value of the square copper complexes (dsp^2 bonds) will approach more closely to the theoretical value of $1.73\mu_B$ than is the case with its tetrahedral complexes or the simple cupric ion. Pauling (*loc. cit.*) has quoted moment values of certain four-coordinated copper complexes which, on the basis of X-ray analysis, are known to possess planar square configuration. But, these instances are unconvincing, and the quoted moment values are of rather doubtful nature. For, these include substances like $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$, $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$, etc., and the moment values quoted for them are stated to lie between 1.79 and 1.87 as reported by some workers. But others (Sugden, *J. Chem. Soc.*, 1932, 164) including ourselves have obtained different and higher moment values for the substances mentioned. Moreover, all chemical and electrochemical considerations lead to the inevitable conclusion that the bonds in these compounds are definitely of the ionic type. The substances like $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ are known to undergo more or less complete dissociation in aqueous solution, giving all the reactions characteristic of simple cupric ions. The planar structure for these molecules, as determined by the X-ray analysis, cannot be regarded as an undoubted evidence about their covalent character. For, as is well known, even the ionic compounds in the crystalline state may give rise to planar configuration, if the radius ratio and the polarization properties of the ions lie within certain limits (cf. Goldschmidt, *Trans. Faraday Soc.*, 1929, 28, 267). Besides, as the ionic bond may resonate with both tetrahedral sp^3 and planar sp^2d bonds (with d -orbital in the same valence shell as s and p), the planar structure found for the above-mentioned copper complexes might as well be attributed to weak covalent bonds of the sp^2d type. These bonds are, therefore, described by some as semi-polar and semi-covalent bonds. The compounds with such bonds, therefore, are to be placed in the class of associated complexes.

An essentially planar covalent structure for a molecule must retain its character unchanged even in solutions. Hence, the conclusion drawn from the X-ray examination alone cannot be the sole criterion for the bond type in complexes.

It was, therefore, expected that a careful magnetic measurement of copper complexes might throw some light on the bond type in these molecules, though not with as much uniqueness as in the case of nickel complexes. With this end in view the measurement of magnetic moment of a large number of copper complexes was undertaken, and the variation of magnetic moment with temperature was also determined in some cases for the sake of exact comparison after allowing for the θ -correction. A few compounds, the moment values of which have been determined by other workers, have also been included in order to make the list as comprehensive as possible.

E X P E R I M E N T A L

The preparation of all the copper complexes under investigation was made with chemically pure substances and the purity of the products was ascertained by the determination of their copper content. The magnetic susceptibility at room temperature of these complexes was measured in a Gouy's balance with a field strength of 10.16×10^3 gauss, taking all the usual precautions described in previous communications. Measurement of susceptibilities at low temperatures was carried out in a special quartz torsion balance using a cryostat of the gas-flow type in which the supply of cold air and liquid air was adjusted by the working of a pump controlled by the automatic operation of a sensitive relay. Temperature in the cryostat could be maintained constant within 1° . The entire apparatus consisting of the torsion balance and the cryostatic arrangement was designed by Dr. A. Bose for his measurements of magnetic properties of paramagnetic crystals at low temperatures at the Indian Association for the Cultivation of Science. A detailed description of the apparatus and its working has been published in the Science Congress Proceedings (1949, Part III, 41). We express our thanks to Dr. A. Bose and Mr. A. Datta for kindly measuring the susceptibilities of some of our substances at low temperatures.

In calculating the magnetic moment for the copper atom in the complex, diamagnetic corrections were made in each case. For susceptibilities of atoms and various structural constants, Pascal's values (corrected) were employed. For ions, the susceptibility values given by Trew (*Trans. Faraday Soc.*, 1941, **37**, 488) were used. The diamagnetic correction for bivalent copper was assumed to be equal to that of bivalent zinc as their ionic radii are almost equal. The values for the latter, as given by Kido (*Sci. Rep. Tohoku Imp. Univ.*, 1933, **21**, 149, 288), is -12.8×10^{-6} . The moment value of the central copper atom is then calculated from the expression, $\mu_n = 2.84 \sqrt{\chi_A \cdot T}$, and from $2.84 \sqrt{\chi_A \cdot (T - \theta)}$ where θ -correction was available from the measurement of susceptibility variation with temperature. The values of θ was obtained by plotting the values of $1/\chi_A$ against the absolute temperature, the intercept of the curve on the temperature co-ordinate giving the value of θ .

D I S C U S S I O N

On arranging the substances under investigation as in the following table with their colours, values of their magnetic moments, and their crystal structure, wherever known, against each, we find that an interesting classification of the complexes into two groups emerges from an analysis of their moment values, more or less in good agreement with their physico-chemical behaviour. The compounds No. 1-17, which are presumably inner-metallic complexes of the penetration type, as revealed by their chemical behaviour, show magnetic moment values closer to the spin moment of one unbalanced electron ($1.73 \mu_B$), particularly when the θ -correction is made. These values, after θ -correction where it has been made, lie more or less between 1.66 and 1.81 μ_B . The remaining compounds, particularly after θ -correction, show more or less an effective moment value of 1.90 to 2.20 μ_B . To this group belong all the copper ethylenediamine

TABLE I

Results of magnetic measurement.

Substance.	Colour.	%Cu.	t in °K.	$\chi_g \times 10^6$.	$\chi_M \times 10^6$.	$\chi_A \times 10^6$.	μ_B .	μ_B corrected for θ .	Remarks.
1. Copper biguanide chloride [Cu(C ₂ H ₇ N ₃) ₂][Cl] ₂ · 2H ₂ O	Rose-red	17.02 calc. 17.06	305	3.249	1204	-131	1335	1.73 $\theta=27$	
2. Copper diethylbiguanide Cu(C ₂ H ₅ N ₃) ₂	Rose-red (1) Violet-blue (2)	16.93 16.85 calc. 16.91	304 304	2.685 2.813	1009 1058	-190 -190	1199 1248	1.71 $\theta=20$ 1.72 $\theta=10$	
3. Copper dimethylglyoxime Cu(C ₄ H ₇ N ₂ O ₂) ₂	Dark brown	21.50 calc. 21.66	304	4.276	1255	-108.7	1363.7	1.80 $\theta=8$	
4. Copper picolinate Cu(C ₆ H ₄ NO ₂) ₂	Violet-blue	20.55 calc. 20.67	299	4.089	1258	-133	1391	1.84 $\theta=37$	Planar (Cox, J. Chem. Soc., 1935, 731; 1936, 775)
5. Copper <i>meta</i> phenylene dibiguanide chloride [Cu(C ₁₀ H ₆ N ₁₀)Cl] ₂ · 3H ₂ O	Red-violet	14.63 calc. 14.53	304	2.640	1150	-169.5	1319.5	1.80 $\theta=30$	
6. Copper biguanide thiocyanate [Cu(C ₂ H ₇ N ₃) ₂](SCN) ₂	Blue-violet	16.67 calc. 16.63	303	3.206	1223	-125	1348	1.82	
7. Copper phenylbiguanide chloride [Cu(C ₈ H ₁₁ N ₃)Cl] ₂ · 3H ₂ O	Red	11.74 calc. 11.72	302	2.018	1095	-249	1344	1.81	

TABLE I (contd.)
Results of magnetic measurement.

Substance.	Colour.	% Cu.	t in °K.	$\chi_g \times 10^6$.	$\chi_M \times 10^6$.	$\delta \times 10^6$.	$\chi_A \times 10^6$.	μ_B .	μ_B corrected for θ .	Remarks.
8. Copper dicyan- diamidine $\text{Cu}(\text{C}_2\text{H}_5\text{N}_4\text{O}_4)$	Rose red		24.04 calc. 23.93	304	4.614	1225	-74	1399	1.78	
9. Copper ethylene- diamine bisacetylacetonone $\text{Cu}(\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}_4)$	Dark violet		22.13 calc. 22.26	305	4.097	1169	-129	1298	1.78	
10. Copper benzoin monoxime $\text{Cu}(\text{C}_{14}\text{H}_{11}\text{NO}_2)$	Green		21.90 calc. 22.02	296	3.978	1148	-137.5	1285.5	1.76	
11. Copper phenylbi- guanide <i>p</i> -sulphonate $\text{Cu}(\text{C}_8\text{H}_{10}\text{N}_5\text{O}_3\text{S})_2$	Violet-red		10.64 calc. 10.71	303	1.793	1064	-219	1283	1.77	
12. Copper phthal- cyanine $\text{Cu}(\text{C}_{17}\text{H}_{12}\text{N}_8)$	Dark blue				1.68	966	-251	1217	1.73 (K)	Planar (Robert- son, <i>J. Chem. Soc.</i> , 1935, 615; 1936, 1195; 1937, 219)
13. <i>bis</i> -Salicylaldehyde propylenediamine copper $\text{Cu}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_4)$	Violet								1.766	
14. Copper ethylene dibiguanide sulphate $[\text{Cu}(\text{C}_8\text{H}_{10}\text{N}_5)]\text{SO}_4$ $\cdot 5.5\text{H}_2\text{O}$	Rose-red		14.64 calc. 14.70	300	2.818	1219	-148	1367	1.82	

TABLE I (contd.)

Results of magnetic measurements

Substance.	Colour.	%Cu.	t in °K.	$\chi_g \times 10^6$.	$\chi_M \times 10^6$.	$\chi_A \times 10^6$.	μ_B .	θ in °K.	μ_B (corr.)	Remarks
15. Copper salicylaldehyde xime $\text{Cu}(\text{C}_7\text{H}_6\text{NO}_2)_2$	Yellowish green	18.90 calc. 18.94	303	3.690	1238	-146	1384		1.84	Planar (Cox., loc. cit.)
16. Copper oxine $\text{Cu}(\text{C}_9\text{H}_6\text{NO})_2$	Dirty yellow	18.02 calc. 18.08	302	3.499	1230	-179	1409	15	1.81	
17. Copper cystine $[\text{Cu}(\text{C}_6\text{H}_{10}\text{N}_2\text{O}_4\text{S}_2)] \cdot 2\text{H}_2\text{O}$	Pale green	18.66 calc. 18.84	300	3.699	1262	-172.5	1434.5	-7	1.89	
18. Copper bispyridine thiocyanate $[\text{Cu}(\text{C}_5\text{H}_4\text{N})_2](\text{SCN})_2$	Violet-blue	18.81 calc. 18.84	305.6	3.807	1285	-158	1443	35	1.77	
19. Copper bisformyl camphor $\text{Cu}(\text{C}_{11}\text{H}_{15}\text{O}_2)_2$	Grass green						1.89 (M)			M = Mellor <i>J</i> <i>Proc. Roy. Soc.</i> N. S. Wales 1942, 76, 138.
20. Copper sulphanilate $\text{Cu}(\text{C}_6\text{H}_4\text{NSO}_3)_2 \cdot 4\text{H}_2\text{O}$	Dark green	13.22 calc. 13.25	297	2.777	1331	-219	1550	15	1.91	
21. Copper phenyl- glycine $\text{Cu}(\text{C}_8\text{H}_8\text{NO}_2)_2$	Blue	17.46 calc. 17.48	298	3.653	1327	-178	1505		1.92	
22. Potassium cupric chloride $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$	Blue	19.99 calc. 19.89	305	4.217	1355	-157	1512	-8	1.95	Planar S = Sugden, loc. cit.
23. Copper bispyridine nitrate $\text{Cu}(\text{C}_5\text{H}_4\text{N})_2(\text{NO}_3)_2$	Blue	18.35 calc. 18.40	300	4.047	1398	-138	1536		1.93	
24. Copper anthranilate $\text{Cu}(\text{C}_7\text{H}_6\text{O}_2\text{N})_2$	Green	18.94 calc. 18.95	303	4.115	1381	-152	1533	10	1.92	

TABLE I (contd.)

Results of magnetic measurements

Substance	Colour	%Cu	t in °K.	$\chi_g \times 10^6$	$\chi_M \times 10^6$	$\delta \times 10^6$	$\chi_A \times 10^6$	μ_B	θ in °K μ_B (corr.)	Remarks
25. Copper quinaldine 8-carboxylate $\text{Cu}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$	Light blue	14.94 calc. 14.94	305	3.116	1324	-213	1537	1.93		
26. Copper quinaldinate $\text{Cu}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$	Green	14.83 calc. 14.94	301	3.148	1302	-212.5	1552.5	1.94		
27. Copper bisethylenediamine thiocyanate $[\text{Cu}(\text{C}_2\text{H}_6\text{N}_2)_2](\text{SCN})_2$	Blue-violet	18.88 calc. 18.95	303	4.065	1366	-171	1537	1.94		
28. Copper tetrapyridine nitrate $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_4](\text{NO}_3)_2$	Blue-violet	14.55 calc. 12.64	303	2.572	1298	-251	1549	1.94		
29. Copper dimethylglyoxime chloride $[\text{Cu}(\text{C}_4\text{H}_8\text{O}_2\text{N}_2)]\text{Cl}_2$	Bright green	25.36 calc. 25.38	303	5.753	1442	-103	1545	1.94	-85	2.2
30. Potassium cuprisalicylate $\text{K}_2[\text{Cu}(\text{C}_7\text{H}_5\text{O}_3)] \cdot 4\text{H}_2\text{O}$	Green	13.08 calc. 13.10	305	2.637	1280	-223.6	1503.6	1.93	0	1.93
31. Copper glycine $[\text{Cu}(\text{C}_2\text{H}_4\text{NO}_2)_2] \cdot \text{H}_2\text{O}$	Deep blue	27.30 calc. 27.46	303	6.228	1430	-97	1527	1.93	-100	2.2
32. Copper tetrammine nitrate $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$	Blue							2.0		Stoner "Magnetism and Matter", 1934, p. 493.
33. bis-Formylcamphor ethylenediamine copper dihydrate $\text{Cu}(\text{C}_{14}\text{H}_{19}\text{O}_2\text{N}_2) \cdot 2\text{H}_2\text{O}$	Wine-red							2.08		Mellor (loc. cit.)

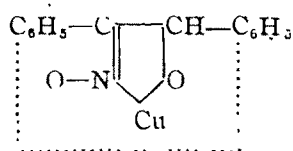
K = Klemm, *J. prakt. Chem.*, 1935, 183, 82, 1939, 165, 73.M = Mellor, *J. Proc. Roy. Soc. N. S. Wales*, 1942, 76, 158.

complexes, copper pyridine complexes, potassium cupric chloride, copper dimethylglyoxime chloride and a few others, which are often regarded as inner metallic complexes, such as copper sulphanilate, copper anthranilate, copper quinaldinate, copper quinaldine 8-carboxylate, copper glycine and copper phenylglycine, etc. Thus, as already referred to in the theoretical part, a distinction between the copper complexes with dsp^2 planar square bonds and those with ionic, sp^3 tetrahedral or sp^2d planar bonds is possible, in spite of the fact that in both types of complexes the paramagnetism of the substance results from the presence of one unpaired electron in the system. The former represents complexes of the penetration type and the latter those of the associated class.

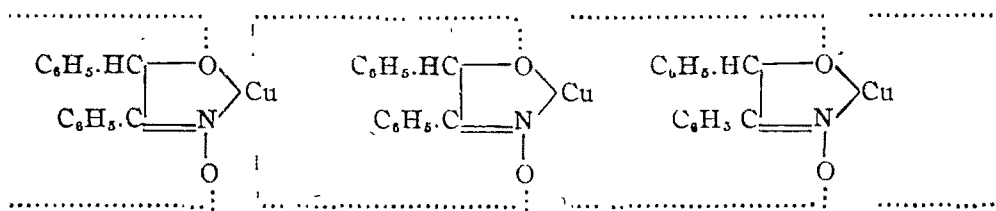
It might be pointed out here that there is yet no evidence for the tetrahedral structure even in the solid state for 4-coordinated copper complexes. All the cupric complexes of either the penetration or the associated type that have yet been examined, are planar. Hence, the bonds in these copper complexes are either of dsp^2 square covalent type, or sp^2d planar feebly covalent type, or predominantly ionic in character. This distinction, though deducible in a general way from their physico-chemical properties, becomes more or less conspicuous from a comparison of their magnetic properties. For instance, copper glycine and copper phenylglycine, which belong to the group of inner-metallic complexes, do not differ much in their physical and chemical properties and in the nature of their co-ordination from copper cystine; but the magnetic measurements show that in the latter the bonds are strongly covalent of the planar dsp^2 type, whereas in the former two they are weakly covalent of the planar sp^2d type, resonating with the ionic structure to a certain extent. This difference may possibly be attributed to the fact that cystine behaves as a four-coordinating or quadrifunctional unit.

There appears to be another significant distinction between these two classes of copper complexes, which expresses itself in their difference of colour. All those cupric complexes in which the bond is predominantly ionic, ion-dipole, or of feebly covalent type (sp^2d or sp^3), *i. e.* all those which are described as normal or associated complexes, are either deep blue, blue, blue-violet, or green in colour; whereas those in which the bond is strongly covalent of the dsp^2 type, classed as penetration complexes, show quite a variety of colours such as red, rose-red, violet-red, violet, greenish yellow, dark brown, and intense dark blue with metallic lustre. The blue colour is thus found in both the groups, whereas red, rose-red, dark brown, yellowish green or greenish yellow are confined only to the strong covalent complexes of the dsp^2 type, described as the penetration complexes. The *bis*-formylcamphor ethylenediamine copper dihydrate, which is wine-red in colour but gives an effective moment value of $2.08 \mu_B$ according to Mellor (*J. Proc. Roy. Soc., N. S. Wales*, 1942, **75**, 168), seems to form the only exception to this. A redetermination of the susceptibility value of this compound in a magnetically pure form and of its temperature variation might possibly lead to a revision of the moment value. This colour distinction in the case of copper complexes, however, is not so sharp as in the corresponding nickel compounds. This is in close agreement with their magnetic distinction. For, as is well known, the two types of nickel complexes, penetration and associated, are clearly distinguished by their opposite magnetic character, the former being diamagnetic with red, yellow or brown colour, and the latter being paramagnetic, with blue or blue-violet colour.

A few individual cases deserve special consideration. The copper benzoin monoxime contains one copper atom for one molecule of benzoin monoxime. Its structure is represented by many by the configuration (I) in which the copper atom is assumed to form rather unusual co-ordination bonds with phenyl groups. The effective moment value of the compound corresponds exactly to the spin moment of one unpaired electron. It resembles in this respect the anhydrous cupric halides, indicating the presence of covalent bonds in four-fold co-ordination. The compound may, therefore, be represented with advantage by the configuration (II) in which the molecule is associated in the form of an unending chain like the anhydrous palladous chloride, the two oxygen atoms of each molecule with their lone pair of electrons supplying the necessary points for co-ordination or attachment with the copper atom of the adjoining molecule.



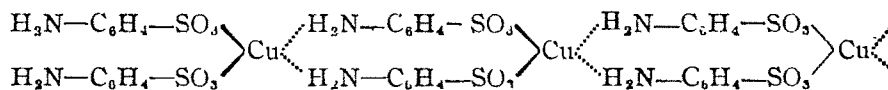
(I)



(II)

The configuration (II) may have either a *cis* or a *trans* arrangement of oxygen and nitrogen atoms around the central copper atom.

Copper sulphanilate, on the other hand, presents a case in which the bond must be regarded either as purely ionic, or, we may assume, as in the previous case, an unending co-ordinated chain structure of associated molecules. The bonds in the latter case, as the magnetic moment shows, will be necessarily of the weak covalent character of sp^2d type. The structure is represented by the configuration (III), which may also be of two isomeric types, *cis* and *trans*, assuming a planar arrangement.



(III)

ORGANIC FUNGICIDES. PART I. SYNTHESIS OF DIBROMOACETAMIDES

BY A. B. SEN AND K. C. JOSHI

Six new dibromoacetamides have been prepared preliminary to evaluation of their fungicidal activity. A new method for preparing dibromoacetic acid and dibromoacetyl chloride is given.

Strong fungicidal activity was observed by Weaver and Whaley (*J. Amer. Chem. Soc.*, 1947, **69**, 515) in some of the bromoacetanilides prepared in their laboratory. They synthesised a number of N-alkyl-bromoacetamides (*loc. cit.*) with a view to studying their fungicidal activity. The corresponding unhalogenated amides and the mono-halogenated paraffins were found to be non-toxic. The fungicidal activity of the bromoamides was therefore attributed to the position of the halogen atom.

The present work has been undertaken to study the modifications in fungicidal activity by increasing the number of halogen atoms in the molecule. It may be expected that such increase may possibly result in increased fungicidal activity as the halogen atom is supposed to be responsible for this property. With this aim in view, a number of analogous dibromoacetamides have been synthesised.

The starting material for the preparation of these amides is dibromoacetic acid. A survey of literature reveals that no satisfactory method is available for its preparation. So far it has been obtained by the action of excess of bromine on boiling acetic acid in the presence of sunlight, sulphur or phosphorus (Perkin and Duppa, *Annalen*, 1858, **108**, 111; Auwers and Bernhardt, *Ber.*, 1891, **24**, 2219; Genvresse, *Bull. Soc. chim.*, 1816, *iii*, **7**, 365). Carius (*Ber.*, 1870, **3**, 336) and Steiner (*Ber.*, 1874, **7**, 506) prepared it by the action of a large excess of bromine on ethyl acetate at 160°. In all these methods, much of the bromine is lost at the high temperature used and the dibromoacetic acid is obtained in low yields, the main product being monobromoacetic acid. Genvresse's method, which involves the heating of acetic acid and 5% sulphur with bromine at 150°, gives only 10% dibromoacetic acid. The present authors have prepared this acid in 88% yield by the decarboxylation of dibromomalonic acid.

The dibromoacetic acid has been converted into dibromoacetyl chloride by the action of thionyl chloride and the dibromoacetamides obtained by the action of different amines on the dibromoacetyl chloride in ether medium.

EXPERIMENTAL

Dibromoacetic Acid.—Dibromomalonic acid was first prepared by the action of bromine in chloroform on malonic acid according to the method of Patrieff (*Ber.*, 1874, **7**, 401). Bromine (165 g.) and chloroform (400 c.c.) were taken in a round bottomed flask fitted with a condenser, the latter being connected to an absorption tower. Finely powdered malonic acid (50 g.) was then added and the whole mass stirred. Gradually the reaction became brisk. The flask was then immersed in ice to control the reaction. When the reaction slowed down, the whole mass was left at room temperature (30°) for 24 hours. It was then refluxed on a water-bath till no more HBr evolved and the

mass was nearly decolorised. It was filtered and washed with chloroform. Dibromomalonic acid was obtained as colourless crystals, m. p. 131° , yield 110 g. (88% theory).

Dibromomalonic acid (110 g.) was decarboxylated at 130° in an oil-bath. The residual liquid was distilled under reduced pressure when a yellow liquid was obtained, b. p. 125° - 135° /10 mm., yield 80 g. (88% of theory). [Found. Br, 73.10; equiv. (neutralisation), 217.7. Calc. for $C_2H_2O_3Br_2$: Br, 73.36 per cent. Equiv., 217.8). This confirms that it is dibromoacetic acid.

Dibromoacetyl Chloride.—Thionyl chloride (80 c.c., 3 moles) was added dropwise to dibromoacetic acid (70 g, 1 mole) under constant stirring at 0° . A vigorous reaction took place and after the reaction had subsided, the mixture was left overnight. It was then refluxed on a water-bath for an hour, the excess of thionyl chloride removed and the residual liquid was distilled under reduced pressure, when it was obtained as an orange-yellow liquid, b. p. 60° - 64° /4 mm., yield 62 g. (82% of theory).

Dibromoacetamides.—Two molecular proportions of the required amine in 15 c.c. of dry ether were taken in a 250 c.c. flask, fitted with a dropping funnel and reflux condenser, and cooled in ice. Dibromoacetyl chloride (one molecular proportion), dissolved in 15 c.c. of dry ether was then added drop by drop. A vigorous reaction took place. The reaction mixture was left overnight and then the ether distilled off. The residual solid was a mixture of the amide and the amine hydrochloride. The latter was removed by treating with water and the remaining solid (amide) was then extracted with ether. The ethereal layer was separated, the ether removed and the compound was recrystallised from a suitable solvent. Most of them have an irritating action on the skin.

The following compounds have been obtained.

Dibromacetamides.

Name of compounds.	M. p.	Yield.	Mol. formula.	% of Nitrogen found. required.	
1. N-Methyl dibromoacetamide	122°	84.6%	$C_3H_5ONBr_2$	5.85	6.06
2. N-Ethyl dibromoacetamide	81°	75.0	$C_4H_7ONBr_2$	5.75	5.72
3. N-n-Butyl dibromoacetamide	76°	86.0	$C_6H_{11}ONBr_2$	4.73	5.12
4. N-Diethyl dibromoacetamide	212°	49.0	$C_8H_{11}ONBr_2$	5.5	5.12
5. N-Dibromoacetanilide	138°	95.0	$C_8H_7ONBr_2$	4.13	4.8
6. N-Dibromoacetyl-phenyl- hydrazine	Does not melt, but decomposes above 200°	92	$C_8H_8ON_2Br_2$	8.85	9.09

CHEMICAL LABORATORIES,
LUCKNOW UNIVERSITY,
LUCKNOW.

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SOME REACTIONS WITH 2-PROPIONYL- α -NAPHTHOL

By A. V. REGE AND S. V. SHAH

Action of sulphur dichloride, thionyl chloride, and sulphuryl chloride on 2-propionyl- α -naphthol has been investigated. Action of chlorine, bromine, nitric acid and diazobenzene chloride on the reaction products has also been studied.

The reactions between benzene and naphthalene derivatives and the chlorides of sulphur viz., sulphur monochloride, sulphur dichloride, thionyl chloride and sulphuryl chloride have been studied by various workers. Recently sulphides of the general formula, R-S-R (where R represents COCH_3 , OH , C_{10}H_7 ; OH , C_{10}H_6 ; OH , COOH , C_{10}H_5 ; etc.) have been obtained by Airan and Shah (*J. Univ. Bom.*, 1940, 9, III, 115).

In the present investigation 2-propionyl- α -naphthol was allowed to react with sulphur dichloride, thionyl chloride and sulphuryl chloride separately using bismuth chloride as a catalyst. It was also considered of interest to see how the reagents like nitric acid and chlorine would react with this naphthol derivative.

Thionyl chloride was allowed to react at 60° as well as at room temperature with 2-propionyl- α -naphthol with the same catalyst in different media (acetic acid, benzene, and ether), but in all cases the original compound was obtained.

The sulphide on treatment with bromine gives a bromo compound, identical with 4-bromo-2-propionyl- α -naphthol (Hantzsch, *Ber.*, 1906, 39, 3097). Thus the position of the sulphur linkage is the same as that of bromine. A chloro compound (m. p. 93°) was obtained by the action of chlorine on the sulphide and it is identical with the chloro compound obtained by the action of sulphuryl chloride or chlorine on 2-propionyl- α -naphthol. Evidently the sulphide linkage is broken by chlorine and the compound is 4-chloro-2-propionyl- α -naphthol.

Similarly the nitro compound obtained from 2-propionyl- α -naphthol by analogy with the above bromo and chloro compounds has been given the structure as 4-nitro-2-propionyl- α -naphthol.

The following conclusions are arrived at :

- (1) 2-Propionyl- α -naphthol does not react with thionyl chloride.
- (2) 2-Propionyl- α -naphthol reacts with sulphur dichloride to give 4: 4'-dihydroxy-3: 3'-dipropionyl-dinaphthyl trisulphide.
- (3) The sulphide obtained is stable towards sulphuryl chloride and acetic anhydride.
- (4) The sulphur linkage is broken by chlorine, bromine, nitric acid and diazobenzene chloride yielding respectively 4-chloro-, 4-bromo-, 4-nitro- and 4-benzeneazo-2-propionyl- α -naphthols.
- (5) The sulphide parts with two atoms of sulphur during the process of benzoylation.
- (6) 2-Propionyl- α -naphthol reacts with sulphuryl chloride, nitric acid and chlorine to give 4-chloro-, 4-nitro- and 4-chloro-2-propionyl- α -naphthol respectively.

E X P E R I M E N T A L

(1) 4:4'-Dihydroxy-3:3'-dipropionyl-dinaphthyl Trisulphide.—To a solution of 2-propionyl- α -naphthol (5 g.) in ether at room temperature was added sulphur dichloride (2 c.c.) using bismuth chloride as a catalyst. Within half an hour a yellow solid separated. It was crystallised from benzene, m. p. 190° . It gave the ferric chloride reaction for the hydroxy group. (Found: S, 19.9. $C_{26}H_{22}O_4S_3$ requires S, 19.45 per cent).

The above sulphide was refluxed with acetic anhydride on a sand-bath for 8 hours and then poured in ice-cold water. The compound on crystallisation from alcohol was found to be identical with the original sulphide. Thus no acetylation of the sulphide could take place.

The sulphide was dissolved in sodium hydroxide solution and benzoyl chloride was added drop by drop. The white compound obtained was washed with sodium hydroxide and then with water. It was crystallised from benzene, m. p. 202° . It contained sulphur. (Found: S, 5.21. $C_{40}H_{30}O_6S$ requires S, 5.01 per cent). Its molecular weight was determined by refluxing a known quantity of the benzoyl derivative with a known excess of potassium hydroxide, the excess of which was then back titrated against standard hydrochloric acid. (Found: M. W., 628.8. $C_{40}H_{30}O_6S$ requires M. W., 638) Thus during the process of benzoylation two atoms of sulphur are shed off.

The sulphide (2 g.) was taken in 25 c.c. of dry benzene. To this 5 c.c. of sulphuryl chloride were added with constant shaking. The reaction mixture was refluxed over a water-bath for about one hour at 60° . It was filtered off and the filtrate was distilled under reduced pressure. No new compound was obtained. The sulphide on the filter paper was identical with the original sulphide. The sulphur linkage is thus stable towards sulphuryl chloride.

4-Chloro-2-propionyl- α -naphthol.—To a solution of the sulphide (5 g.) in acetic acid dry chlorine was passed with constant shaking. Immediately a solid came out. It was crystallised from alcohol, m. p. 93° and found to be identical with chloro compound obtained from 2-propionyl- α -naphthol by the action of sulphuryl chloride. It showed the absence of sulphur and the presence of the hydroxy group. (Found: Cl, 15.40. $C_{13}H_{11}O_2Cl$ requires Cl, 15.14 per cent). Chlorine, thus breaks the sulphur linkage.

4-Bromo-2-propionyl- α -naphthol.—Compound (1) was suspended in acetic acid and bromine was added dropwise till the solid went into solution. A crystalline compound was obtained after half an hour, m. p. 98° and it showed the presence of bromine and the hydroxy group and the absence of sulphur. It showed the absence of bromine in the side-chain. (Found: Br, 29.11. $C_{13}H_{11}O_2Br$ requires Br, 28.67 per cent). Mixed melting point with the compound prepared according to the method of Hantzsch (*loc. cit.*) gave no depression.

4-Nitro-2-propionyl- α -naphthol.—To a solution of the sulphide (5 g.) in acetic acid (25 c.c.) nitric acid (d 1.42) diluted to 10 c.c. with acetic acid was added with constant shaking. After the reaction was over the whole reaction mixture was poured in water and the solid compound was removed and crystallised out of alcohol, m. p. 158° . It showed the presence of nitrogen and the hydroxy group and the absence of sulphur.

Thus the position of the nitro group was confirmed by the absence of sulphur. (Found: N, 6.01. $C_{13}H_{11}O_4N$ requires N, 5.71 per cent).

4-Benzeneazo-2-propionyl- α -naphthol.—The sulphide was dissolved in sodium hydroxide solution and ice-cold solution of diazobenzene chloride, prepared according to the method of Shah *et al.* (*J. Univ. Bom.*, 1943, 11, V, 85), was added with constant shaking. A brown dye was obtained which showed the absence of sulphur and was identical with 5-benzeneazo-2-propionyl- α -naphthol, prepared according to Goldzweig and Keiser (*J. prakt. Chem ii*, 43, 96). It melted at 110°.

(2) 4-Chloro-2-propionyl- α -naphthol.—To a solution of 2-propionyl- α -naphthol (4 g.) in ether was added sulphuryl chloride (3 c.c.) in the presence of bismuth chloride (catalyst). A vigorous reaction was started and within a couple of minutes a solid compound separated. It was crystallised from alcohol. It gave positive ferric chloride reaction and showed the absence of chlorine in the side-chain. (Found: Cl, 15.41. $C_{13}H_{11}O_2Cl$ requires Cl, 15.14 per cent).

To a solution of 2-propionyl- α -naphthol (5 g.) in acetic acid dry chlorine was passed with constant shaking. A solid came out which was crystallised from alcohol, m. p. 93° and was found to be identical with the above compound (mixed m. p.). Its constitution is proved by its formation from the sulphide with known constitution.

(3) 4-Nitro-2-propionyl- α -naphthol.—2-Propionyl- α -naphthol (5 g.) taken with acetic acid (25 c.c.) in a conical flask and 3 c.c. of nitric acid (d 1.42) diluted to 10 c.c. with acetic acid was added to it. There was reaction in the cold with evolution of brown fumes. A yellow solid came out. It was filtered and crystallised from alcohol, m. p. 158°. It contained hydroxy group and nitrogen. It was found to be identical with the above compound (No. 2) and gave no depression in the mixed melting point. Its constitution is proved by its formation from the sulphide of known constitution.

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CHEMISTRY LABORATORY,
RAJARAM COLLEGE,
KOLHAPUR.

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A NOTE ON THE ACTION OF CHLORINE AND BROMINE ON
2-ACETYL-1-NAPHTHOL AND OF BROMINE ONLY
ON 2-HYDROXY-3-NAPHTHOIC ACID

By A. V. RAGE AND S. V. SHAH

Hantzsch (*Ber.*, 1906, **39**, 3097) obtained by the action of bromine on 2-acetyl-1-naphthol a monobromo derivative in which bromine had entered into the naphthalene nucleus, whereas Ullmann (*Ber.*, 1897, **30**, 1468) had obtained a bromo derivative in which the hydrogen of acetyl only was replaced by a bromine atom. By the action of chlorine in excess on the same compound, the present authors have obtained a tetrachloro derivative, trichloromethyl-2-(1-hydroxy-4-chloro)-naphthyl ketone and by the action of bromine in excess dibromomethyl-2-(1-hydroxy-4-bromo)-naphthyl ketone. By the action of bromine in excess on 2-hydroxy-3-naphthoic acid, a dibromo derivative has been obtained, whilst Gradenwitz (*Ber.*, 1894, **27**, 2622) obtained only a monobromo derivative.

Trichloromethyl-2-(1-hydroxy-4-chloro)-naphthyl Ketone.—When 2-acetyl-1-naphthol (5 g.) in acetic acid (50 c.c.) is treated with excess of dry chlorine till the product turns yellow and then poured into water, a yellow solid separates out which on crystallisation from alcohol melts at 141° . [Found: Cl, 15.21; equiv. (Ba salt), 232.9. $C_{12}H_7O_4Cl$ requires Cl, 14.17 per cent. Equiv., 250.5].

Dibromomethyl-2-(1-hydroxy-4-bromo)-naphthyl Ketone.—When 2-acetyl-1-naphthol is heated to 110° in an oil-bath and bromine (25 c.c.) is added dropwise, white fumes of hydrogen bromide are evolved and a yellow solid separates out. It is washed first with dilute sodium thiosulphate solution and then with water and crystallised from chloroform, m. p. 201° . (Found: Br, 57.28. $C_{12}H_7O_4Br_2$ requires Br, 56.74 per cent). When refluxed with NaOH solution, the bromine in the side-chain is decomposed and bromine in the filtrate from the decomposed product estimated. (Found: Br, 38.24. $C_{12}H_7O_4Br_2$ requires Br, 37.83% for two bromine atoms in the acetyl group).

1:6-Dibromo-2-hydroxy-3-naphthoic Acid.—The acid (5 g.) taken with acetic acid (50 c.c.) is treated with bromine (15 c.c.) with constant shaking. On cooling the product crystals appear. They are washed with dilute sodium thiosulphate solution and crystallised from alcohol, m. p. 251° . (Found: Br, 46.10; equiv., 342.6. $C_{11}H_6O_5Br_2$ requires Br, 46.24 per cent. Equiv., 346.0]. The product on oxidation with alkaline $KMnO_4$ solution for 6 hours on a sand-bath, concentrated, acidified, and then extracted with ether gives a white solid, m. p. 168° , identical with 4-bromophthalic acid. (Found: equiv., 120.1. $C_8H_5O_4Br$ requires equiv., 122.5).

ON THE FORMATION AND STABILITY OF BICARBONATES OF THE METALS OF THE GROUP II OF THE MENDELEEF'S PERIODIC TABLE

By K. C. GROVER

The acid carbonates of Be, Mg, Zn, Cd and Hg have been isolated for the first time in the solid state, and have also been stabilized. The stability of the bicarbonate of Zn, Cd and Hg (II B group) decreases with decreasing electro-positive character of these metals.

In group II of the Mendeleef's Periodic Table, Keiser and co-workers (*J. Amer. Chem. Soc.*, 1908, 30, 1711) investigated only the acid carbonates of calcium and barium, and Haider, Aziz and Langer (*J. Indian Chem. Soc.*, 1944, 21, 178) that of strontium. They succeeded in isolating the solid compounds at a lower temperature and found them to possess the compositions $\text{CaCO}_3 \cdot 1.75 \text{H}_2\text{CO}_3$; $\text{BaCO}_3 \cdot 1.5 \text{H}_2\text{CO}_3$ and $\text{SrCO}_3 \cdot 1.60 \text{H}_2\text{CO}_3$. In order to advance the study of these compounds of the remaining elements of the group, the acid carbonates of Be, Mg, Zn, Cd and Hg have been investigated. Mostly these exist in solution only and at low temperatures.

However, Haider *et al.* (*loc. cit.*) claimed to have found a method of stabilizing the bicarbonates of strontium and lithium. The method was tried in the case of the bicarbonates, under investigation, and it was found that a certain degree of stabilisation could be attained.

EXPERIMENTAL

The bicarbonates of the elements—Be, Ba, Sr, Zn and Cd—being less soluble in water are precipitated from their aqueous solutions, while the bicarbonates of Ca, Mg and Hg are less soluble in alcohol in the presence of which they are precipitated.

The bicarbonates of Be, Mg, Zn, Cd and Hg were therefore prepared by mixing solutions of potassium bicarbonates with the corresponding chlorides of the metals, all cooled to 0° . It was observed that Hg $(\text{HCO}_3)_2$ was precipitated only by the addition of alcohol to the mixed solution and for precipitating Mg $(\text{HCO}_3)_2$, a large quantity of absolute alcohol was required. The precipitates were washed successively with ice-cold water, saturated with CO_2 , alcohol and ether, and dried at 0° .

A. The decomposition temperature of each of the above precipitates was found by gradually raising the temperature of the ice-cold water-bath inside which the boiling tube containing the precipitate was placed. The decomposition temperature was recorded when the CO_2 evolved from the precipitate on passage through a little lime water just turned the latter turbid.

TABLE I

No.	Bicarbonates.	Decomposition temperature		
		without gelatin.	with 5% gelatin.	with 2% gelatin.
I	Be $(\text{HCO}_3)_2$	7°	10°	13°
II	Mg $(\text{HCO}_3)_2$	5°	8°	10°
III	Zn $(\text{HCO}_3)_2$	11°	14°	18°
IV	Cd $(\text{HCO}_3)_2$	5°	8°	11°
V	Hg $(\text{HCO}_3)_2$	2°	5°	7°

From above, it is found that the decomposition temperatures of these bicarbonates are raised

- (i) by the presence of gelatin and,
- (ii) by increasing concentration of gelatin.

B. The ratio of CO_2 to the oxide in these precipitates was determined by the method of Keiser and MacMaster (*J. Amer. Chem. Soc.*, 1908, **30**, 1715) as improved by Haider *et al.* However, a few modifications were made such as :—

(a) A sulphuric acid tower was interposed between the bottle containing water (to dissolve vapours of HCl gas) and the tube for absorption of CO_2 . The function of this sulphuric acid tower is to dry the CO_2 on its passage to the saphnolite tube where it is to be absorbed.

(b) Saphnolite was substituted for a solution of potash and was found to be a better absorbent of CO_2 . This did away with the possibility of the formation of potash solution from potash bulbs being sucked by the suction applied, when potash bulbs were used for absorbing CO_2 .

(c) A weighed calcium chloride tube was fitted after saphnolite tube in order to absorb any moisture coming from saphnolite, thus checking any source of error liable to be caused by any moisture contained in the saphnolite itself.

(d) Suction was applied after the experiment in order to drive out any CO_2 left in the bottle containing water.

The ratio of CO_2 to that of oxide determined as above, in each case, was found to be as follows :—

(i) $\text{Be}(\text{HCO}_3)_2$	$\text{CO}_2 : \text{BeO} = 2.62$
(ii) $\text{Mg}(\text{HCO}_3)_2$	$\text{CO}_2 : \text{MgO} = 2.20$
(iii) $\text{Zn}(\text{HCO}_3)_2$	$\text{CO}_2 : \text{ZnO} = 2.74$
(iv) $\text{Cd}(\text{HCO}_3)_2$	$\text{CO}_2 : \text{CdO} = 2.72$
(v) $\text{Hg}(\text{HCO}_3)_2$	$\text{CO}_2 : \text{HgO} = 2.10$

An alternative determination of the ratio CO_2 : oxide in a solution of the acid carbonate of each of these metals by the turbine method (after Langer) gave the same values as above.

The formulae derived for these bicarbonates on the basis of these observations and calculations are as follows :

- (i) $\text{Be}(\text{HCO}_3)_2$. 0.65 CO_2 .
- (ii) $\text{Mg}(\text{HCO}_3)_2$. 0.20 CO_2 .
- (iii) $\text{Zn}(\text{HCO}_3)_2$. 0.74 CO_2 .
- (iv) $\text{Cd}(\text{HCO}_3)_2$. 0.72 CO_2 .
- (v) $\text{Hg}(\text{HCO}_3)_2$. 0.10 CO_2 .

The net increase in weights was calculated in the case of the carbonates of all these metals after keeping them to constant weights firstly in an atmosphere of CO_2 and mois-

ture and secondly over calcium chloride. The results show that bicarbonate formation by the direct absorption of CO_2 by the carbonates of the metals of Group II does not occur in the case of beryllium, magnesium, strontium and zinc, but takes place to a slight extent in the case of calcium (19.09%), barium (9.63%), cadmium (8.65%) and mercury (7.23%), which values, no doubt, are far below the theoretical absorption necessary for the formation of bicarbonates.

A stable form of the bicarbonate of these metals was prepared by precipitating a solution of the respective carbonate in carbonated water, containing galatin, by means of absolute alcohol. These precipitates did not decompose at the ordinary temperature of the laboratory, while the other preparations rapidly decomposed above their respective decomposition temperatures. It is desirable to extend this method of stabilisation to other unstable compounds.

CHEMICAL LABORATORY,
GORAKHPUR INTERMEDIATE
COLLEGE, GORAKHPUR, U P.

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A NOTE ON MIXED INDICATORS IN ALKALIMETRIC TITRATION

By K. V. S. KRISHNAMURTY

Simpson (*Ind. Eng. Chem.*, 1924, **16**, 709) introduced a great simplification in the titration of carbonate to the bicarbonate stage with his new mixed indicator consisting of 6 parts of Thymol blue and 1 part of Cresol red. It seemed of interest to investigate if other indicators of this type may be found. Amongst many combinations tried, the following have yielded useful results. In a few cases the end-point is much more sharp than with Simpson's indicator. Aliquot parts of a $N/10$ solution of pure sodium carbonate, obtained by heating Analar sodium carbonate to constant weight at 300° for 2 to 4 hours, were titrated to the bicarbonate stage; then varying quantities of solid bicarbonate were added to the carbonate solution and the carbonate was determined by titration to the bicarbonate stage. The results are tabulated below. In all cases two or three drops of the indicator were added and the liquid diluted to 100 ml.

TABLE I

Soln. taken = 30 ml. of $N/10\text{-Na}_2\text{CO}_3 \equiv 15$ ml. of $N/10\text{-HCl}$.

Indicator strength = 0.1%

Indicator.	Initial colour.	Colour at end-point.	Vol. of $N/10\text{-HCl}$ required (average)	Remarks
1. Simpson's	Purple	Rose	15.00 ml.	Sharp
2. Tropoelin 000 No. 1 & Malachite green (1:1)	Dark purple	Bluish green or green	15.00	Very sharp
3. Tropoelin 000 No. 1 & Thymol blue (1:1).	Pink	Orange	15.05	Not very sharp, slow.
4. Thymol blue & Phenol red (1:1)	Dark pink	Orange	15.00	Sharp
5. Thymol blue & Neutral red (1:1)	Purple blue	Light orange to yellow	15.05	Fairly sharp

Experiments (not quoted here) show that sodium carbonate may be very conveniently titrated in the presence of a large excess (even 20 times) of bicarbonate down to all concentrations up to $N/200$. With small amounts (2 ml.) of the carbonate solution the results are very irregular. Any quantity above 5 ml. gives accurate results. Indicator No. 2 falls strictly under the category of screened indicator. Further work is in progress on the determination of pK values for these indicators.

The author's best thanks are due to Dr. Bh. S. V. Raghava Rao of the Andhra University for suggesting the work and taking further interest.

STUDIES IN SESQUITERPENES. PART V. THE ESSENTIAL OIL FROM THE OLEO-RESIN OF *HARDWICKIA PINNATA*

BY SUKH DEV AND P. C. GUHA

The essential oil from the oleo-resin of *Hardwickia pinnata* has been shown to consist of humulene (α -caryophyllene), β -caryophyllene and a cadinenic sesquiterpene

Hardwickia pinnata (N. O. Caesalpiniaceae) is a very large and handsome tree found in the evergreen forests of Western Ghats from South Kanara to Travancore. It is also known as the Malabar Mahogany (Kanada: Yenñemara; Tamil: Enneykolavu; Malayalam: Shurali; Marathi: Anjana). It grows to a height of about 100 ft. with a trunk of about 4 to 8 ft. in diameter. Its wood is moderately hard and yields a valuable timber: the sapwood is spacious and the heartwood is dark red or reddish brown, exuding a red, sticky resin (Kirtikar and Basu, "Indian Medicinal Plants", 2nd Ed., p. 882; Iyer and Sudborough, *J. Indian Inst. Sci.*, 1918-20, 2, 29).

The tree, when tapped, yields a dark oleo-resin. The yield of the resin is about 4 to 16 gallons for a single tree. Sometimes a tree is found which yields no oil at all (Trotter, *Manual of Indian Forest Utilization*", 1940, p. 289). Though the oleo-resin has the smell and taste of Copaiba, its characteristics are sufficiently distinct to prevent any confusion (Hooper, *Pharm. J.*, 1907, 24, 4).

The balsam of *Hardwickia* has been used in India for the treatment of Gonorrhoea (Kirtikar and Basu, *loc. cit.*). The resin exuding from the heartwood is used for dressing the sores of elephants (Rama Rao, "Flowering Plants of Travancore", 1914, p. 142).

According to Weigel (*Phar. Zentr.*, 1906, 47, 773), the oleo-resin contains 48.5% of volatile oil, 48.3% of resin acids and 3.2% of resene. Schimmel and Co. (Reports, April 1905, and April 1907) got 44% of the oil. Iyer and Sudborough determined the percentage of the volatile oil as 43 to 47%. The latter authors prepared caryophyllene alcohol from the oil by Wallach and Walker's method (*Annalen*, 1892, 271, 288). They also prepared a nitrosochloride of m.p. 161° (α -caryophyllene nitrosochloride, m.p. 175°), and a nitrosate, m.p. 153-54° (α -caryophyllene nitrosate, m.p. 162°) and concluded that the oil chiefly consisted of α -caryophyllene and that the β -caryophyllene was absent. But as is evident from the comparison of the m.p. of the derivatives given above, their derivatives were not sufficiently pure and as such their conclusion about the presence of α -caryophyllene was based on unsound grounds. Further, their statement about the absence of β -caryophyllene is erroneous in view of the facts now established.

In order to study the constituents of the volatile oil, we have steam-distilled two lots of the oleo-resin obtained from the Tinnevely district in May, 1946 and October, 1947. It

has been found that the yields of the essential oil and the relative proportions of the chief constituents vary considerably with the season. The first sample gave us only 26% of the oil, which boiled over a comparatively wide range. The second specimen yielded 48.3% of oil consisting mostly of the lower-boiling sesquiterpenes. The essential oil obtained from the 2nd lot of the oleo-resin has been investigated fully.

The oil has a characteristic resinous odour and a pungent bitter taste. The oil as obtained on steam-distillation from a large copper still has a clear, green colour, but the redistilled oil is colorless. Its various constants are given in Table I and have been compared to those recorded by other investigators.

The oil on careful and repeated fractionation furnished six fractions. The physical properties of the various fractions obtained are recorded in Table II. A survey of these properties indicates that the oil consists entirely of bicyclic sesquiterpenes. This has been confirmed by the analyses of the separate fractions.

Fraction I, which constitutes about 80% of the oil, has been shown to consist essentially of β -caryophyllene. The presence of this hydrocarbon was established by the preparation of the characteristic blue nitrosite, m.p. 110° . The m.p. of the compound as given in the literature is 115° (Deussen, *Annalen*, 1907, 356, 13). Since we were unable to raise the m.p. of our product, an authentic sample of β -caryophyllene nitrosite was prepared from genuine caryophyllene (B.D.H.) which also melted at 110° , and did not depress the m.p. of our product. The fraction also yielded β -caryophyllene alcohol on hydration with Bertram-Walbaum reagent. Further, the presence of the hydrocarbon was confirmed by the preparation of caryophyllene dihydrochloride in a 60% yield. The physical constants, especially the optical rotation, of the fraction III agree more closely with those recorded for β -caryophyllene. This fraction yielded the dihydrochloride in practically the same yield, but the nitrosite was obtained in about double the yield. This indicates that probably the fraction I contains another strongly laevo-rotatory hydrocarbon capable of yielding the same dihydrochloride. It is not unlikely that some γ -caryophyllene is present in the oil, but its presence could not be confirmed by the preparation of its nitrosochloride.

Fig. 1

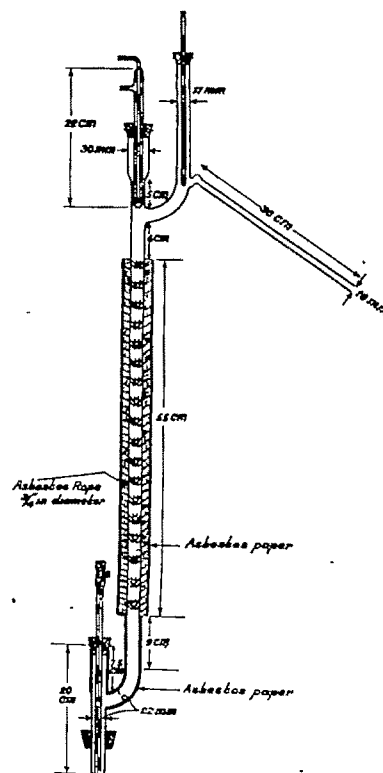


TABLE I

Constants.	Present sample.	Schimmel and Co. (<i>loc. cit.</i>)	Iyer and Sudborough (<i>loc. cit.</i>) Travancore. Mysore.
<i>d</i>	0.9045 ^{30.8°}	0.9062 ^{15°}	0.931 ^{15°} 0.908 ^{15°}
<i>n</i>	1.4949 ^{30.8°}	—	1.500 ^{20°} 1.500 ^{20°}
[α] _D	-9.4	+7.42°	-1.72° -7.86°
Acid value	Nil	0.85	Trace Trace
Sapon. value	Nil	2.88	Nil Nil
Acetyl value	Nil	—	12.6 1.4

Ruzicka and Zimmermann (*Helv. Chim. Acta*, 1935, **18**, 219) made the interesting observation that the caryophyllene mixture as obtained from clove oil was capable of reacting with maleic anhydride in benzene to yield a crystalline adduct (m. p. 98°) corresponding to about 50% of the terpene. Since the chief constituent of the caryophyllenes is supposed to be β -caryophyllene, it is considered likely that the product has originated from this hydrocarbon, which, however, does not contain a conjugated system of double bonds. A careful reinvestigation of the problem by Ruzicka, Plattner and Balla (*ibid.*, 1941, **24**, 1219) revealed that the compound is probably formed by diene synthesis by addition to a relatively strongly laevo-rotatory monocyclic sesquiterpene. They examined several different samples of caryophyllene and found that the yields of the adduct were highly variable, and that samples giving higher yields of the dihydrochloride gave poor yields of the maleic anhydride addition product.

The reaction of maleic anhydride with fraction I has also been studied. But the hydrocarbon did not give the product of m.p. 98°. Instead, another crystalline product of m.p. 179-80° was isolated in a poor yield. The substance is under investigation. This supports Ruzicka's results that the adduct of m.p. 98° is not derived from β -caryophyllene.

Fraction V does not yield any picrate-forming material on dehydrogenation with selenium and also does not give the blue nitrosite. The fraction consists chiefly of humulene (α -caryophyllene), as shown by the preparation of the crystalline nitrosochloride and nitrosate.

Fraction VI gave cadalene and a trace of an unidentified azulene on dehydrogenation with selenium. *l*-Cadinene dihydrochloride was obtained in a poor yield by passing dry HCl gas through its ethereal solution. The fraction is slightly dextro-rotatory and does not give the characteristic colour reaction of cadinene. The cadinenic hydrocarbon present in this fraction may be either *d*-cadinene or some other sesquiterpene capable of giving cadinene dihydrochloride.

EXPERIMENTAL

All melting and boiling points are uncorrected.

The Oleo-resin.—The oleo-resin was collected by the courtesy of the Forest Range Officer, Ambasamudrum, Tinnevely, in August 1947 and was received by us in October,

1947. The specimen was a thick, viscid liquid of a dark brown (almost black) colour. When viewed in thin layers, the oleo-resin looked transparent and was of a greenish yellow colour. It had a characteristic odour which was not unpleasant.

Fractionation of the Essential Oil

The oleo-resin (29 lbs.) was steam-distilled from a large copper still, when 14 lbs. (48.3%) of a light green oil were obtained. The oil was dried over anhydrous sodium sulphate and distilled from an ordinary Claisen's flask under vacuum. The oil was obtained as a colorless, mobile liquid, b.p. 100° - $105^{\circ}/2$ mm. (125° - $129^{\circ}/10$ mm.). The various constants of the redistilled oil, as recorded in Table I, were determined by standard procedures. The oil was carefully fractionated in vacuum first at 2 mm. The various fractions, thus obtained, were then systematically and repeatedly fractionated at 30-40 mm. in order to have sharper cuts. A final distillation of each fraction was carried out at 2 mm. over sodium. The results of the fractionation are given in Table II.

A fractionating column of the partial-condensation take-off type, as illustrated in Fig. 1, was used. Various types of packings, including single-turn copper helices made from 18 B.S. gauge copper wire, were tried, but flooding could not be controlled; hence the column was indented (Vigreux type). Asbestos rope $\frac{3}{4}$ " in diameter was wound round the column which was finally covered with several rounds of asbestos paper, to serve as insulation. The column is a slight modification of the one described by Thompson ("Organic Syntheses", Vol. XX, p. 96; cf. Morton, "Laboratory Technique in Organic Chemistry", pp. 73-97). The column was operated at a maximum reflux ratio so that there was just no flooding. The rate of distillation was maintained at about 0.5 c.c./min. The reflux ratio was adjusted by the manipulation of the dephlegmator and by wrapping or unwrapping some cotton wool over the portion of the column just above the insulation. The oil was heated in a metal bath with proper control of the bath temperature.

The oil (3000 g.) on fractionation gave seven fractions (vide Table II) on which different physical measurements were made.

TABLE II

No.	B.p.	Weight.	%Yield.	d_{40}^{20}	n_D^{30}	$[\alpha]_D^{24}$	MR _D .
I	$150^{\circ}/36$ mm. $100^{\circ}/2$	233.8 g.	77.9	0.8976	1.4940	-10.5	66.09
II	$150-52^{\circ}/36$	86.0	2.9	—	—	—	—
III	$152-53^{\circ}/36$	176.0	5.9	0.8990	1.4955	-9.3	66.17
IV	$153-55^{\circ}/36$	20.0	0.6	—	—	—	—
V	$155-57^{\circ}/36$	93.0	3.1	0.8997	1.4960	-6.0	66.19
VI	$114-15^{\circ}/3$	80.0	2.6	0.9026	1.4990	+0.5	66.32
VII	Residue	80.0	2.6	—	—	—	—
	Loss	127.0	4.2	—	—	—	—

Identification of β -Caryophyllene

The evidence for the identification of β -caryophyllene in *Hardwickia pinnata* oil are summarised in Table III.

The Nitrosite.—The fraction I (10 c. c.) was dissolved in petroleum ether (10.0 c.c., b.p. 60°–80°) and an aqueous saturated solution of sodium nitrite (10.0 c. c.) was added. The mixture was chilled in ice and salt mixture to below –10° and glacial acetic acid (10 c. c.) was introduced slowly under shaking during 10 to 15 minutes. The petroleum ether layer slowly turned blue and towards the end blue needles started separating out. The reaction mixture was kept in the ice-bath for another 15 minutes and the crystals that separated out were filtered off and washed with a little petrol and further purified by recrystallising twice from dilute alcohol in long, blue needles, m.p. 110° with effervescence. Yield from fraction I, 1.4 to 1.6 g. (10–12%); fraction III gave nearly double this yield.

Further recrystallisations of the product from dilute alcohol or petroleum (b.p. 40°–60°) failed to raise the melting point.

TABLE III

Properties.	β -Caryophyllene.	Fraction I.	Fraction III.
B.p.	103°–103.5°/4 mm*.	100.0°/2 mm.	102–103°/2 mm.
Density	d_{20}^{20} , 0.9075*	d_{20}^{20} , 0.8976	d_{20}^{20} , 0.8990
Ref. index	n_D^{20} , 1.4995**	n_D^{20} , 1.4940	n_D^{20} , 1.4955
Optical rotation $[\alpha]_D$	–8.16*	–10.5	–9.3
%C.	88.16 (calc.)	88.01	88.23
%H.	11.84 (calc.)	11.90	11.75
M.p. of nitrosite.	115.0°, (110.0°)**	110.0°	110.0°
M.p. of dihydrochloride	69–70°†	68.9°	68–69°
M.p. of β -caryophyllene alcohol	94–96°††	95–96°	95–96°

* Navés and Perrottet, *Helv. Chim. Acta*, 1941, 24, 789.

** The m.p. 110° is of the product prepared by the authors from genuine caryophyllene. Deussen (*Annalen*, 1907, 388, 13) has recorded the m.p. as 115°.

† Schreiner and Kremers, *Pharm. Arch.*, 1899, 2, 296; 1902, 4, 164.

†† Wallach and Walker, *Annalen*, 1892, 271, 288; Asahina and Tsukamoto, *J. Pharm. Soc. Japan*, 1922, 463; *Chem. Abst.*, 1922, 16, 3312.

The mixed melting points of the nitrosite, dihydrochloride and β -caryophyllene alcohol, prepared from genuine caryophyllene (B.D.H.) with the corresponding derivatives prepared from these fractions, were 110° , $68-69^\circ$ and $95-96^\circ$ respectively.

The Dihydrochloride.—The hydrocarbon (10.0 g.) was mixed with anhydrous ether (10 c.c.) and cooled in an ice-salt bath (-20°). The well-cooled solution was saturated with dry HCl gas and the practically colorless solution thus obtained was kept in the freezing mixture for 16 hours. The solvent and the excess of the HCl gas were sucked off in vacuum with a feeble current of dry air being passed through it. The residual syrup was chilled in a freezing mixture (-20°) for $\frac{1}{2}$ an hour with occasional scratching, when the product solidified. This was taken up in 7 c. c. of ether and 15 c. c. of alcohol were added. The clear solution was chilled as before for $\frac{1}{2}$ an hour. The white crystals were filtered off and washed with a little cold alcohol. The product was recrystallised from alcohol and ether in the same way, as white needles, m.p. $68-69^\circ$, yield 50-60%.

β -Caryophyllene Alcohol.—The fraction I (10 g.) was mixed with 98% acetic acid (20 g.) and 50% sulphuric acid (1 g.). The reaction mixture was heated at $50^\circ-60^\circ$ for 8 hours. The dark violet reaction mixture was poured into excess of water and the crude acetyl β -caryophyllene alcohol was extracted with ether and then hydrolysed with alcoholic potash by refluxing for 2 hours. The hydrolysed product was worked up in the usual manner with ether. The solvent was removed and the residue was fractionated in vacuum. The β -caryophyllene alcohol distilled at $120^\circ-125^\circ/1$ mm. The distillate which had crystallised out was recrystallised from petrol ether ($40^\circ-60^\circ$) at 10° to a constant melting point as white silky needles, m.p. $95-96^\circ$ (cf. Bertram and Walbaum, *J. prakt. Chem.*, 1894 ii, 49, 1; Wallach and Walker, *loc. cit.* Asahina and Tsukamoto, *loc. cit.*).

Reaction with Maleic Anhydride.—The fraction did not give the colour reaction with diazotised *p*-nitroaniline (Fieser's test for conjugation: Fieser and Campbell, *J. Amer. Chem. Soc.*, 1938, 60, 168; cf. Goodway and West, *J. Chem. Soc.*, 1939, 1855). β -Caryophyllene as isolated from clove oil gives an orange-brown colour in a few minutes (Naves and Perrottet, *loc. cit.*).

A mixture of the terpene (25 g.), maleic anhydride (15 g.) and dry benzene (75 c. c.) was refluxed for 24 hours. A clear yellow solution resulted. The solvent was removed under a slight vacuum and the residue was fractionated at a low pressure. Maleic anhydride distilled over first, followed by the unreacted terpene (18 g., 72%). A higher boiling fraction, b.p. $180^\circ-200^\circ/2$ mm. (4.0 g.) was obtained and a polymer was left in the flask. The fraction (b.p. $180^\circ-200^\circ/2$ mm.) was obtained as a syrup which crystallised on trituration with light petrol. The crystals were filtered off and recrystallised from a mixture of benzene and petrol, m.p. $177-80^\circ$. Further recrystallisation from the same mixture of solvents raised the m.p. to $179-80^\circ$ with slight shrinking at $177-78^\circ$. The product was obtained in white silky needles, yield 0.6 g. (cf. Ruzicka, Plattner and Balla, *loc. cit.*).

Identification of Humulene

The evidences for the presence of humulene in the essential oil from *Hardwickia pinnata* oleo-resin are summarised in Table IV.

TABLE IV

Properties	Humulene*.	Fraction V.
B p.	263°-266°	155°-57°/36 mm.
Density	d_{18}° , 0.9001	d_{30-8}° , 0.8997
Refrac. index	n_{19}° , 1.5021	n_{20-8}° , 1.4960
Optical rotation	Inactive	-60
M.p. of nitrosate	163°, 161°	160°
M.p. of nitrosochloride	176°; 174°**	175°
M.p. of nitrolpiperidide	153°	153°

* Chapman, *J. Chem. Soc.*, 1895, 87, 54, 780; 1928, 785.

† Simonsen and Todd, *ibid.*, 1942, 191.

The Nitrosate.—The terpene (10 c.c.) was dissolved in glacial acetic acid (10 c.c.) and freshly prepared (undistilled) *iso*-amyl nitrite (11.0 c.c.) was added. The resulting green solution was chilled in an ice-salt-bath. A well-cooled mixture of glacial acetic acid (10 c. c.) and conc. nitric acid (d 1.42; 10 c. c.) was then slowly added to the above solution with shaking. The temperature was not allowed to go beyond 0°. After 15 minutes 50 c. c. of alcohol were added and the clear green solution was left aside in the ice-bath for 3 to 4 hours. The white solid which had separated out was filtered off, washed with some cold alcohol and dried. The product was recrystallised several times from a mixture of benzene and alcohol as fine silky needles, m.p. 160° with decomposition.

Nitrosochloride.—A well-cooled alcoholic solution of HCl gas (20 c. c.) was added slowly to a chilled mixture of the hydrocarbon (20 c. c.), absolute alcohol (20 c. c.), ethyl acetate (20 c. c.) and *iso*-amyl nitrite (20 c. c.). The deep bluish green mixture was left in the ice-bath for an hour and was then kept at room temperature for another 2 hours. The white crystalline solid was filtered off and washed with ice-cold alcohol. The product was repeatedly crystallised from a mixture of chloroform and benzene till the m.p. became constant. The product was obtained in colorless prisms, m.p. 175° (decomp.), yield 5.0%.

The Nitrolpiperidide was prepared by the action of piperidine on the nitrosochloride in the usual manner. The compound was recrystallised from dilute alcohol as fine white needles, m.p. 153°.

Presence of a Cadinenic Sesquiterpene

Dehydrogenation.—The fraction VI (2.0 g.) and selenium (4.0 g.) were heated together at 300°-315° for 32 hours when the evolution of hydrogen selenide had practically

ceased. In the beginning the reflux slowly acquired a deep blue colour, which vanished towards the end. The product was worked up in the usual manner. The cadalene was identified as its picrate, m.p. 114-15°. Mixed m.p. with an authentic sample remained undepressed.

Dihydrochloride.—The fraction VI (1 c. c.) was dissolved in dry ether (1 c. c.) and saturated with dry HCl gas at below 0° and the mixture kept at 0° for 24 hours. The ether and the excess gas were then sucked off and the residue was taken up in 1 c. c. of ethyl acetate. The solution was chilled to -10° and seeded with a speck of cadinene dihydrochloride when crystals began to separate out. After sometime the product was filtered off and recrystallised from ethyl acetate in white needles, m. p. 117-118°. Cadinene dihydrochloride, m.p. 117-118°, did not depress the m.p.

ORGANIC CHEMISTRY LABORATORIES,
DEPARTMENT OF PURE AND APPLIED CHEMISTRY,
INDIAN INSTITUTE OF SCIENCE, BANGALORE.

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INFLUENCE OF HEAT ON THE CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF GUM ARABIC

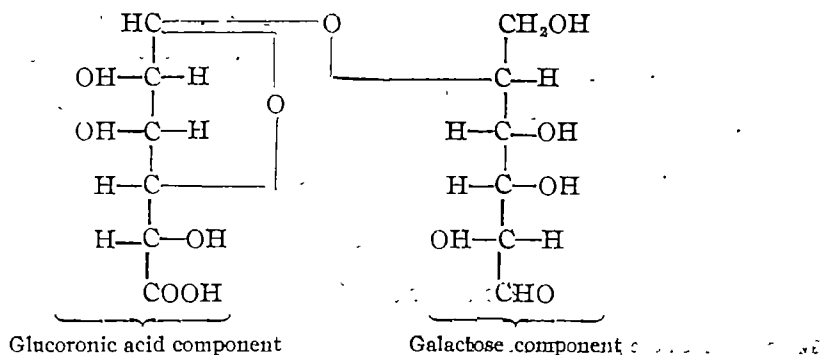
BY M. N. MOORJANI AND C. S. NARWANI

Gum arabic, heated to 170°, when put into water, swells up to a considerable extent, but does not dissolve and the gel thus formed is non-sticky. There is practically no change in the chemical composition of the gum. The insolubility of the gum at 170° is explained to be due to complete dehydration at this temperature and the consequent removal of protective aqueous films surrounding the micelles or the primary particles of the micelles.

The viscosity of the gum solutions goes on increasing to a great extent as the gum is heated from 100° to 160°. The increase in viscosity is due to the increase of imbibed water in gum micelles. Water appears to be oriented in a shell surrounding the gum micelles and thus the disperse phase becomes highly solvated which results in the increase of viscosity.

Action of NaOH on the gum arabic, heated to different temperatures (110°-170°), has been studied potentiometrically.

Gum arabic, an acid polysaccharide, is mainly a calcium salt of arabic acid, the nucleus of which is aldobionic acid (galactose-glucuronic acid) to which sugar molecules of galactose, arabinose and methylpentose are attached. The structure of the aldobionic acid is given below.



Gum arabic, heated to 170°, when put into water, swells up to a considerable extent, but does not dissolve and the gel thus formed is non-sticky. The object of the present work was to study the change in the chemical composition and physical properties of gum arabic on heating it in dry state to various temperatures above 100° and to investigate the action of NaOH on gum arabic heated to different temperatures (110°-170°) by back potentiometric titrations with 0.02N-HCl.

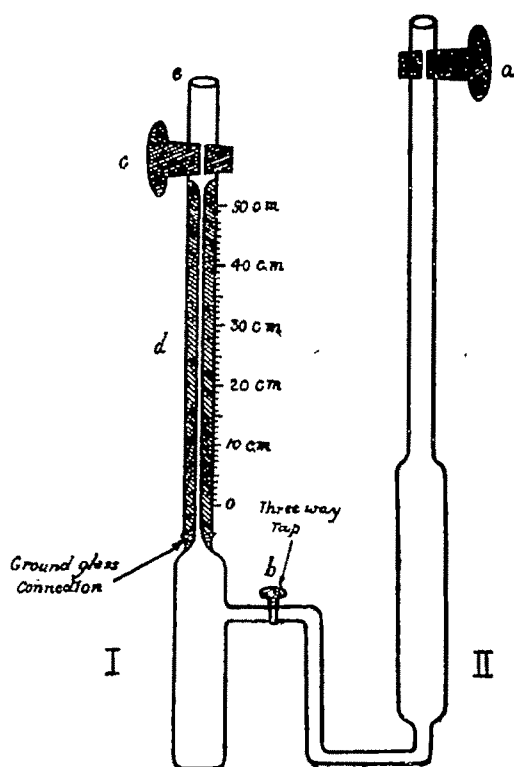
EXPERIMENTAL

The gum arabic used for the experiments had the following composition: pento-
san, 34.34%; galactan, 33.93%; moisture, 13.53%; calcium, 0.6459%.

Arabic acid was prepared from gum arabic by electro-dialysis through cellophane. The acid thus prepared was dried on a water-bath, powdered and sieved through a fine mesh.

Dilatometer Measurements.—The hydration of gum arabic, heated to different temperatures, was investigated in a dilatometer which is diagrammatically represented in Fig. 1.

FIG. 1



The tablets were placed in the left part (I) of the dilatometer. The right part (II) was filled with distilled water free from air and CO_2 by turning the three-way tap (b). The dilatometer was then placed in a thermostat to ensure constancy of temperature of $37^\circ \pm 0.1^\circ$. After half an hour the left side was evacuated through (e) and afterwards the left part of the dilatometer and part of the capillary (d) were filled with air-free distilled water by opening taps (a) and (b). After closing the three-way tap (b), the dilatometer was ready for measurement and the initial reading on the scale attached to the capillary was immediately taken. The final reading was taken when the level in the capillary was constant for about an hour.

TABLE I

Loss of moisture on heating the gum.

Temp. to which the gum was heated	...	110°	120°	130°	140°	150°	160°	170°
% Loss of moisture	...	10.38	11.47	11.94	13.32	13.65	13.65	13.73

TABLE II

Comparative results of the relative viscosity of gum solutions at 37°.

Temp. to which the gum was heated.	Relative viscosity of the gum solutions.					
	6%.	4.5%	3%.	2.5%.	1.5%.	0.75%.
100°	3.480	2.944	2.328	2.087	1.644	1.289
110°	3.772	3.131	2.409	2.168	1.672	1.284
120°	4.018	3.318	2.578	2.306	1.793	1.349
130°	4.13	3.451	2.702	2.418	1.889	1.455
140°	4.415	3.624	2.762	2.478	1.991	1.611
150°	5.898	4.76	3.596	3.174	2.357	1.775

TABLE IIIA

Comparative quantities of 0.02N-NaOH required to neutralise the acidity of 25 c.c. of 8% solution of gum, heated to various temperatures, were found by back potentiometric titrations with 0.02N-HCl (the p_H values were determined by using hydrogen electrode of the Bunker's type).

Temp. to which gum was heated.	0.02N-HCl reqd. to neutralise the excess of NaOH.	0.02N-NaOH reqd. to neutralise the acidity of 2 g. of gum.	Temp. to which gum was heated.	0.02N-HCl reqd. to neutralise the excess of NaOH.	0.02N-NaOH reqd. to neutralise the acidity of 2 g. of gum.
110°	19.45 c.c.	4.55 c.c.	150°	14.3 c.c.	10.7 c.c.
120°	19.1	5.9	160°	12.8	12.2
130°	17.45	7.55	170°	10.7	14.3
140°	16.95	8.05			

TABLE IIIB

Arabic acid on drying at 110° becomes insoluble.

Temp. to which arabic acid was heated.	0.1N-HCl reqd. to neutralise the excess of NaOH.	0.1N-NaOH reqd. to neutralise the acidity of 2g. of acid.
100° (dehydrated)	7.8 c.c.	17.2 c.c.
170° (")	7.4	17.6

7.8 C.c. of 0.1N-HCl are required to neutralise the excess of NaOH, i.e., 17.2 c.c. of 0.1N-NaOH neutralise the acidity of 2 g. of arabic acid. The equivalent weight comes out to be 1162 which is quite in agreement with Thomas and Murray (*J. Phys. Chem.* 1928, 32, 676) who found equivalent weight of arabic acid as 1177. The results are also in accordance with Lucien Amy (*Ann. Chim.*, 1934, ix, 2, 287) who found that on dehydration arabic acid was converted into metagummic acid (of about the same acidity) which again was converted into arabic acid on treatment with NaOH.

TABLE IV

Hydration of gum arabic by dilatometer.

Area of the cross section of the capillary = 0.0115 cm.

Temp. to which the gum was heated.	Fall in the capillary per 1 g. of the gum.	Contraction in vol. per 1 g. of the gum.	Temp. to which the gum was heated.	Fall in the capillary per 1 g. of the gum.	Contraction in vol. per 1 g. of the gum.
110°	11.69 cm.	1.345 c.c.	150°	21.78 cm.	2.505 c.c.
120°	13.99	1.609	160°	22.81	2.623
130°	18.67	2.147	170°	24.02	2.763
140°	19.66	2.261			

DISCUSSION

Gum arabic, heated to 170° , when put into water, swells up to a considerable extent, but does not dissolve; the gel thus formed is non-sticky. There is practically no change in the chemical composition of gum arabic on heating it as determined by the estimations of arabinose and galactose. The insolubility of gum in water can be explained to be due to complete dehydration at 170° and the consequent removal of protective aqueous films surrounding the micelles or the primary particles of the micelles, consequently some of the molecules or molecular groups approach so closely that when they are again brought in contact with water, their attraction for water molecules or its ions is unable to separate them. This is similar to the behaviour of gelatin which, when dried at 130° , becomes insoluble due to dehydration. Alexander (*J. Amer. Chem. Soc.*, 1921, **43**, 438) attributes the insolubility of gelatin to the close approach of its constituent particles.

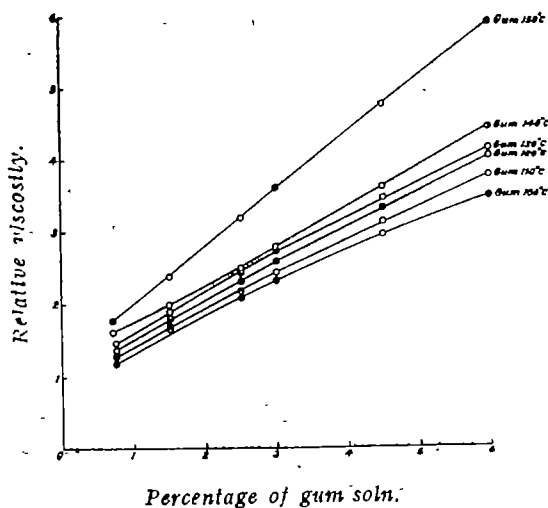
Insoluble gum swells in water to a jelly-like mass which does not dissolve. According to Procter and Wilson (*J. Phys. Chem.* 1928, **32**, 692) the force which causes swelling of gum is an osmotic force, i. e., the diffusion of water through a membrane. In this case the membrane is the arabate ions or aggregates, and the forces which limit the swelling are the cohesive forces existing between the arabate ions.

It was observed by means of the dilatometer (Table IV) that there is contraction in the total volume of water when the dehydrated gum is brought in contact with water, an evidence that water is imbibed by the gum. The water of this hydration layer has a higher density than free water. Thus the adsorbed water is under a high internal force which is due to the polarising effect of the polar groups of the gum molecules on water dipoles and hence the fall in the capillary of the dilatometer. The first suggestion that water exists in colloids in a state different from that of water, as we know it is in bulk, was made by Balcar, Sansum and Woodyatt (*Arch. Internal. Med.*, 1919, **24**, 116). They suggested a theory that there exists a bound \rightleftharpoons free water equilibrium. On heating, the equilibrium is disturbed, more and more free water is lost with the result that more amount of water will be taken up by gum-micelles that have been heated to higher temperature when placed in contact with water. Svedburg (*J. Amer. Chem. Soc.*, 1924, **46**, 2673) finds in the case of gelatin that more and more water is taken up by gelatin as the initial content of water in it is low. From our results of dilatometer measurements, we find that the amount of water taken up by gum-micelles goes on increasing with rise of temperature.

Table II (Fig. 2) shows that the viscosity of gum solutions goes on increasing to a great extent as the gum is heated from 100° to 160° . The increase in viscosity may be explained by the fact that viscosity of a solution is a function of the volume of the solute in solution or what is the same thing, a function of free volume of the solvent. The free volume is the difference between the volume occupied by the gum molecules and that of the solution. The increase in the viscosity is therefore perhaps due to increase in imbibed water. Water appears to be oriented in a "shell" surrounding the gum

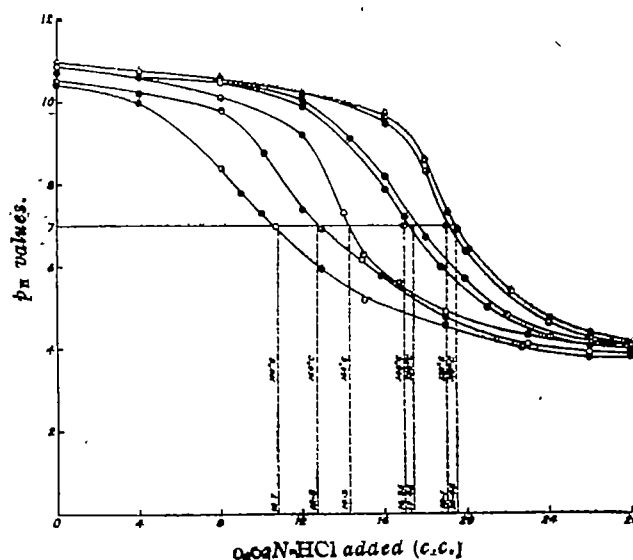
micelles and thus the disperse phase becomes highly solvated which results in the increase of viscosity. This is in accordance with a view put forward by Gortner that dispersion medium is strongly attracted by the disperse phase, so that the disperse phase

FIG. 2



becomes highly solvated, the particles of disperse phase become surrounded by "shells" of the dispersion medium, the apparent viscosity of the system is greatly increased. This view is further confirmed from the results of dilatometer by means of which we find that volume contractions increase with the temperature to which the gum has been heated.

FIG. 3



Action of NaOH on the gum arabic, heated to different temperatures, 110° - 170° , was studied potentiometrically. The quantity of NaOH required for reaching the neutral point goes on increasing with rise of temperature as seen from Table III (Fig. 3). This phenomenon is explained on the basis of difference between the ionisation of calcium and sodium arabates and due to the different hydration of calcium and sodium ions as found by Briggs(*J. Phys. Chem.*, 1931, **35**, 1929) that "with colloids in equilibrium with water, the degree of hydration of the colloid is determined largely, if not entirely, by the number of cations or anions which may be produced from it and that the sodium caseinates are nearly 100 per cent ionised as compared to calcium caseinates which are about 20 per cent ionised". On addition of NaOH, gum arabic, which is a calcium salt of arabic acid, is converted into sodium arabate which gets dissociated to a much greater extent than calcium arabate; hydration of sodium ion being greater than calcium ion, the sodium arabate becomes highly hydrated. Since a lot of water is imbibed by sodium and arabate ions, there is a decrease in free solvent and hence there is an increase in H-ion concentration. The increase in acidity with rise of temperature is due to the fact that on heating, the power to imbibe water goes on increasing as observed from viscosity and dilatometric measurements. Another possible explanation for the increase of acidity of the gum is that the unit of the complex structure of the micelles undergoes a strengthening of cationic linkages releasing bound 'COOH' groups.

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D. J. SIND COLLEGE,
KARACHI.

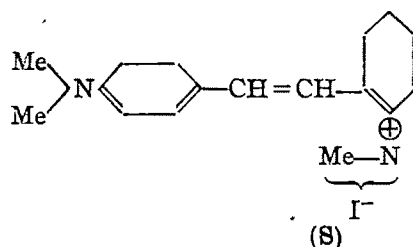
Received June 14, 1948.

THE CYNAINNE DYES OF THE PYRIDINE SERIES. PART VI

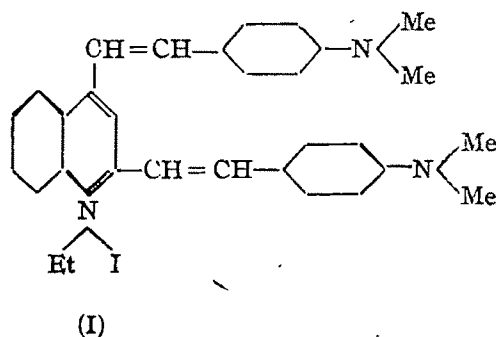
BY M. Q. DOJA AND KAILASH BIHARI PRASAD

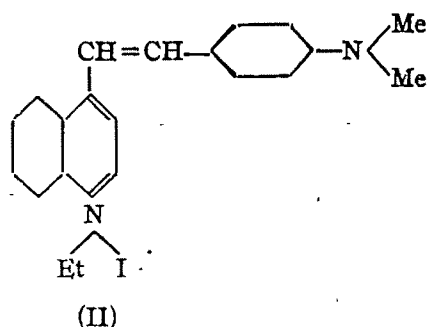
2:6-Dimethylpyridine methiodide and 2:4:6-trimethylpyridine methiodide have been condensed with *p*-dimethylamino- and *p*-diethylaminobenzaldehydes, and the chemical, dyeing and photographic properties of the resulting compounds investigated. The influence of multiplication of *p*-dialkylamino residues on the sensitising power of certain cyanine dyes has been examined.

Mills and Pope (*J. Chem. Soc.*, 1922, 121, 946) prepared the photographic sensitiser having the constitutional formula (S)



and it was found to have very useful photo-sensitising properties. The effect of change of the alkyl radical attached to the tertiary and quaternary nitrogen atoms, and the acid radicals, on the photographic characteristics of the compound, has been studied in this laboratory and reported in previous papers (Doja, *J. Indian Chem. Soc.*, 1940, 17, 347; Doja and Prasad, *ibid.*, 1942, 19, 125; *idem.*, 377; *ibid.*, 1946, 23, 177). The influences of the change in the position of attachment of the *p*-dialkylaminobenzaldehyde residue to the pyridine ring has also been reported (Doja and Prasad, *ibid.*, 1947, 24, 301). Bloch and Hamer (*Phot. J.*, 1930, 54, 374) have studied the effect of introducing two *p*-dimethylaminostyryl residues (I) in a quinaldine nucleus and have compared the sensitisation of this dye with that containing only one *p*-dimethylaminostyryl residue (II).





They have found that the sensitising effect of (I) is not superior to that of (II). In fact, the relative speed of (II) is greater than that of (I).

It was thus of interest to investigate the effect of introducing more than one *p* dialkylaminobenzaldehyde residues into the mononuclear (pyridine) class of cyanine dyes. For this purpose, 2:6-dimethylpyridine methyl iodide and 2:4:6-trimethylpyridine methyl iodide have been condensed with *p*-dimethyl- and *p*-diethylaminobenzaldehydes and the resulting dyestuffs examined. In this way two sets of two compounds ('M' and 'N') and ('E' and 'F') have been prepared. The first set, 'M' and 'N' has been obtained by the condensation of *p*-dimethylaminobenzaldehyde with 2:4:6-trimethyl- and 2:6-dimethylpyridine methyl iodide and the second set, 'E' and 'F', by the condensation of *p*-diethylaminobenzaldehyde with the same two pyridine derivatives, respectively. Table I shows some of the important properties of these compounds.

It is remarkable that both the dimethylamino compounds ('M' and 'N') have higher melting points than the corresponding diethylamino derivatives ('E' and 'F'). The yields of the products in the case of 'N' and 'F' are satisfactory but in the other two cases, they are comparatively poor. The yields of the crude products in all cases were good but they fell after recrystallisation.

Mills and Pope (*Phot. J.*, 1920, **44**, 255) observed that solutions of carbocyanines were decolorised by acidification with mineral acids. The dyestuffs under discussion further confirm the above observation, as their alcoholic solutions are decolorised by the addition of mineral acids. The "relative resistance to decolorisation" shown in Table I, has been determined by finding the value of *N*/100-HCl solution required to decolorise 2 c.c. of 1/100,000 solution of the dyes, and dividing the figures thus obtained by the smallest among these. Thus, it is seen that the dimethylamino dyes are more resistant to decolorisation than the diethylamino dyes.

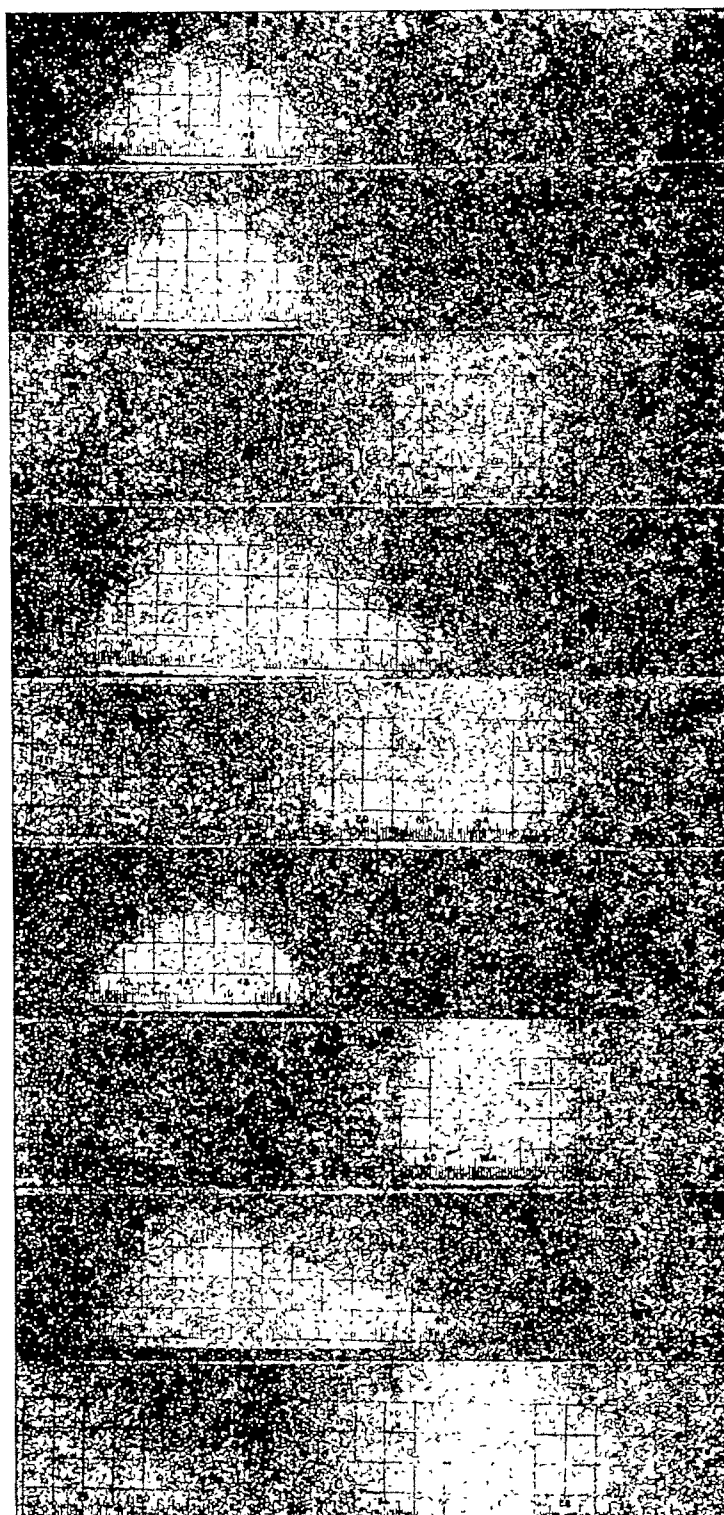
It is also noteworthy that both the tri-styryl derivatives are dull-coloured powders, whereas the di-styryl derivatives form extremely beautiful shining crystals. All these compounds are soluble in acetic acid, chloroform and nitrobenzene. 'E' and 'F' are freely soluble in methyl and ethyl alcohols but 'M' and 'N' dissolve only moderately in these solvents. All the four dyes are sparingly soluble in benzene and ligroin, and insoluble in water and petroleum ether.

Both the dimethyl- and the diethylamino compounds form ruby-red solutions, the latter giving a deeper shade. The "relative intensity" of colour in alcoholic solutions

TABLE I

Compound.	Colour and shape of crystals.	M.p.	Yield.	Reflex.	Pleochroism, one position.	Pleochroism, \perp position.	Relative resistance to decolorisation in alcoholic solution.	Relative intensity of colour in solution.	Extra sensitisation Ranges.	Maximum.
M	Greenish grey powder	234°	37.4%	Nil	Yellowish grey (weak)	Bright yellow	4.65	1.64	5100-5800Å	At about 5300Å
N	Shining green rhombs	254°	51.7	Strong yellowish green	Light grass green	Orange red	2.06	1.00	5100-6400	5400
E	Grey powder	202°	25.0	Nil	Yellowish white	Nearly opaque	1.40	1.79	5100-5600	At about 5400
F	Dirty green crystals	232°	74.06	Strong bottle green	Dirty white	Cherry red	1.00	2.12	5100-6500	5800

M = 2:4:6-Tri-(*p*-dimethylamino)-styryl-pyridine methyl iodide.N = 2:6-Di-(*p*-dimethylamino)-styryl-pyridine methyl iodide.E = 2:4:6-Tri-(*p*-diethylamino)-styryl-pyridine methyl iodide.F = 2:6-Di-(*p*-diethylamino)-styryl-pyridine methyl iodide.



Unbathed plate.

Sensitisation.

} M

Absorption.

} N

} E

} F

(1/10,000) determined in the usual way, by means of a Duboscq colorimeter is given in Table I. The diethylamino compounds, as also visually seen, have a higher intensity value.

The fluorescence of weak alcoholic solutions (1/100,000) of these dyes is given in Table II (cf. Doja, *loc. cit.*).

TABLE II

Wallace colour filter No.	Colour of the fluorescent beam seen at right angles to the incident beam.			
	M.	N.	E.	F.
1	Rose-red	Dull yellow	Weak yellow	Dull yellow
2	Faint pink	Pink	Weak red	Weak red
3	Cherry-red	Weak yellow	Claret-red	Reddish yellow
4	Crimson red	Reddish yellow	Cherry-red	Pink
5	Rose-red	Reddish yellow	Ruby-red	Yellowish red
6	Ruby-red	Greenish yellow	Yellowish red	Orange
7	Lemon-yellow	Yellow	Reddish yellow	Lemon-yellow
8	Dull yellow	Grass green	Light absorbed	Claret-red
9	Light absorbed	Light absorbed	Very weak red	Yellowish pink
10	Crimson-red	Reddish yellow	Ruby-red	Yellowish red

The colour produced on silk, wool and cotton, when dyed with these compounds, is shown in Table III. They are not useful as dyestuffs. Neither the shades are good, nor are they fast either to sunlight or to washing.

The absorption spectra of alcoholic solutions (1/1000) of these dyestuffs taken in a Wedge-spectrograph are shown in Figure 1. They are characteristic of this class of compounds.

TABLE III

Compound.	Colour produced on		
	Silk.	Wool.	Cotton.
M	Weak yellowish blue	Mauve	Weak bluish red
N	Saffron	Dirty magenta	Weak magenta
E	Weak brinjal blue	Weak mauve	Reddish blue
F	Weak orange-yellow	Orange-yellow	Dull yellow

The sensitisation spectra are also shown in the same figure. They demonstrate that the multiplication of dialkylamino residues in a cyanine dye does not necessarily increase the sensitising power of the dyes. In the case under consideration, distyryl derivatives are better sensitisers than their tristyryl analogues (cf. Block and Hamer, *loc. cit.*). Salient features of the sensitisation spectra are given in Table I.

EXPERIMENTAL

2:4:6-Trimethylpyridine methiodide.—2:4:6-Trimethylpyridine, prepared by the method of Hantzsch (*Annalen*, 1882, 215, 1), was quaternised with methyl iodide in a sealed tube by heating on a water-bath for 4 hours. It was recrystallised from methyl alcohol, m. p. 205°. (Found: I, 48.18. $C_9H_{14}NI$ requires I, 48.29 per cent).

2:4:6-Tri-(*p*-dimethylamino)-styryl-pyridine methyl iodide (M).—2:4:6-Trimethylpyridine methyl iodide (0.526 g.), *p*-dimethylaminobenzaldehyde (0.894 g.), piperidine (8 drops) and absolute alcohol (10 c.c.) were heated to a brisk boil under reflux on a water-bath for 12 hours. The reaction mixture developed a light orange colour in the cold; on heating the colour deepened and solid began to separate out. On cooling, the mother-liquor was filtered off and the residue crystallised four times from methyl alcohol, yield 0.49 g. (Found: N, 8.4; I, 19.29. $C_{38}H_{41}N_4I$ requires N, 8.53, I, 19.23 per cent).

2:4:6-Tri-(*p*-diethylamino)-styryl-pyridine methyl iodide (E).—2:4:6-Trimethylpyridine methyl iodide (0.526 g.), *p*-diethylaminobenzaldehyde (1.026 g.), absolute alcohol (10 c.c.) and piperidine (8 drops) were refluxed together for 12 hours. No solid separated out; only a pasty mass was obtained. It was kept in a refrigerator for 48 hours. The paste was scratched vigorously with a glass rod, when it solidified. The solid was recrystallised 4 times from methyl alcohol, yield 0.37 g. (Found: N, 7.57; I, 17.10. $C_{42}H_{53}N_4I$ requires N, 7.56; I, 17.16 per cent).

2:6-Dimethylpyridine methyl iodide.—2:6-Lutidine (10.7 g.) and methyl iodide (14.2 g.) were taken in a sealed tube and heated on the water-bath for 4 hours, and the solid thus obtained was recrystallised from methyl alcohol, yield 16.2 g. (Found: I, 50.89. $C_8H_{12}NI$ requires I, 51.0 per cent).

2:6-Di-(*p*-dimethylamino)-styryl-pyridine methyl iodide, (N).—2:6-Lutidine methyl iodide (1.245 g.), *p*-dimethylaminobenzaldehyde (1.49 g.), absolute alcohol (10 c.c.) and piperidine (5 drops) were heated briskly for 12 hours. The solid which separated out was recrystallised twice from nitrobenzene, yield 15 g. (Found: N, 8.12; I, 24.78. $C_{28}H_{30}N_3I$ requires N, 8.21; I, 24.85 per cent).

2:6-Di-(*p*-diethylamino)-styryl-pyridine methyl iodide, (F).—2:6-Lutidine methiodide (1.245 g.) *p*-diethylaminobenzaldehyde (1.770 g.), absolute alcohol (10 c.c.) and piperidine (5 drops) were boiled under reflux on a water-bath for 12 hours. The mother-liquor was filtered off and the dye crystallised twice from pure methyl alcohol, yield 2.1 g. (Found: N, 7.32; I, 22.31. $C_{30}H_{32}N_3I$ requires N, 7.40; I, 22.40 per cent).

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SCIENCE COLLEGE,
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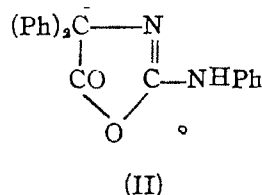
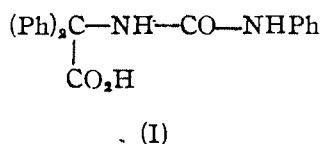
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REACTION OF BENZIL WITH SUBSTITUTED UREA IN PRESENCE OF ALKALI

By T. N. GHOSH

The reaction of benzil with substituted urea in presence of alkali has been studied and the compounds isolated have been characterised.

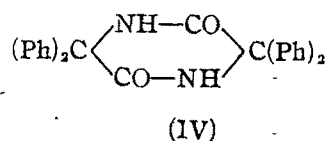
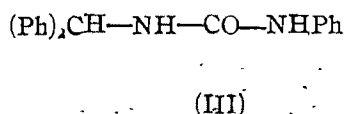
In a previous communication (Sikdar and Ghosh, this *Journal*, 1948, 25, 109) the mechanism of the reaction in which benzil is allowed to react with urea in presence of alkali to yield 5 : 5-diphenylhydantoin has been investigated and outlined. In order to establish such a mechanism it has been considered desirable to extend the reaction with substituted urea derivatives. It has now been found that benzil reacts with monophenylurea in presence of alkali to yield the compounds (I) and (II)



The observation, now made with regard to the non-reactivity of symmetrical diphenylurea towards benzil in presence of alkali, confirms the structure (I) of the compound in which the amino group of monophenylurea has reacted with the hydroxy group of benzilic acid. The compound (I) is acidic in nature and is readily soluble in aqueous sodium bicarbonate.

The compound (II), which is insoluble in cold dilute alkali and is readily hydrolysed by alkali to (I), is also obtained by treating (I) with acetic anhydride, and is identical with the compound obtained by fusing monophenylurea with benzilic acid at 180°-190° (Eberly and Dains, *J. Amer. Chem. Soc.*, 1936, 58, 2546). Eberly and Dains (*loc. cit.*), however, assigned to this compound the structure, 3-phenyl-5 : 5-diphenylhydantoin, which appears to be untenable because such a compound containing -NH-CO- grouping in the ring should be soluble in cold dilute alkali. The analogous thio compound, namely, 3-phenyl-5 : 5-diphenylthiohydantoin (cf. Eberly and Dains, *loc. cit.*) is readily soluble in cold dilute alkali.

When treated with 20% alkali, the compound (I) furnishes a mixture of (III) and a compound to which the structure (IV) is tentatively assigned.



The compound (IV), which is a derivative of 2:5-diketopiperazine and is stable towards hot concentrated hydrochloric acid or 25% alkali, is evidently formed by the hydrolysis of (I) to diphenylamidoacetic acid, $(\text{Ph})_2\text{C} \begin{matrix} \text{NH}_2 \\ \text{CO}_2\text{H} \end{matrix}$, which then forms the cyclic double acid amide (IV) (cf. Kossel, *Ber.*, 1891, **24**, 4149). The constitution of (IV) is supported by analytical data, molecular weight determination and also by the fact that the compound yields diacetyl and di-sodium derivatives.

When, however, the compound (I) is treated with 15% hydrochloric acid, a mixture of (II) and (IV) is obtained.

It is now observed that benzoic acid does not react with monophenylurea in presence of alkali, which lends additional support to the mechanism as outlined previously (cf. Sikdar and Ghosh, *loc. cit.*) with regard to the reaction between benzil and urea in presence of alkali to furnish 5:5-diphenylhydantoin.

EXPERIMENTAL

Reaction of Benzil with Monophenylurea in presence of alkali: Formation of Phenylcarbamidodiphenylacetic Acid (I) and 2-Phenylamino-4:4-diphenyl-5-keto-4:5-dihydro-oxazole (II).—(a). Caustic soda (2 g.), dissolved in water (8 c.c.), and alcohol (95%, 6 c.c.) were added to powdered benzil (3 g.). After 15 minutes monophenylurea (3.5 g.) was added and the mixture was allowed to stand at room temperature for 20 hours with occasional stirring. The reaction mixture was diluted with water to 500 c.c., when a solid was precipitated. It was filtered, washed with water and crystallised from alcohol in colorless rectangular plates (II, 0.8 g.), m.p. 203-204°. (Found: N, 8.29. $\text{C}_{21}\text{H}_{16}\text{O}_2\text{N}_2$ requires N, 8.53 per cent). It is insoluble in cold dilute alkali and is dissolved when boiled with 10% caustic soda solution. The alkaline solution, on acidification with concentrated hydrochloric acid, yields a compound confirmed to be identical with (I), described below. This compound (II) has been found to be identical with the one prepared by Eberly and Dains (*loc. cit.*) by fusing monophenylurea with benzoic acid at 180°-190°.

The alkaline filtrate, described above, was acidified with hydrochloric acid, when a precipitate was obtained, which was filtered, washed with water and was crystallised from alcohol in colorless rectangular plates (I, 1.5 g.), m.p. 180° (decomp.). It was dried at 100°-110° *in vacuo* and then analysed. (Found: N, 7.88. $\text{C}_{21}\text{H}_{16}\text{O}_2\text{N}_2$ requires N, 8.09 per cent). It is readily soluble in aqueous sodium bicarbonate with effervescence.

(b). When the above reaction mixture, after addition of monophenylurea, was heated under reflux for 2 hours, only the compound (I) was isolated, yield 2.8 g.

Attempt to react Benzil with sym-Diphenylurea in presence of Alkali.—Caustic soda (2 g.), dissolved in water (8 c.c.), and alcohol (95%, 6 c.c.) were added to powdered benzil (3 g.). After 15 minutes, *sym*-diphenylurea (5.5 g.) was added and the mixture was then heated under reflux on the water-bath for 4 hours. The reaction mixture

was cooled and then diluted with water to 250 c.c., when a solid was precipitated which was identified to be *sym*-diphenylurea. From the alkaline filtrate a solid was obtained on acidification, which was identified to be benzilic acid.

No reaction was found to take place even when the mixture was allowed to stand at room temperature for 20 hours without being heated.

Action of Acetic Anhydride on compound (I): Formation of compound (II).—The compound (I, 5 g.) was treated with acetic anhydride (30 c.c.) and fused sodium acetate (5 g.), when considerable heat was developed. The reaction mixture was then heated under reflux for 6 hours, cooled and then poured into cold water with stirring. A semi-solid mass was obtained which gradually solidified. It was filtered, washed with water and crystallised from alcohol (charcoal) in colorless, rectangular plates (1 g.), m.p. 203-204°. Its identity with the compound (II), described previously, was confirmed by mixed m.p. and also by analysis.

Action of Alkali on compound (I): Formation of 1-Phenyl-3-diphenylmethylurea (III) and 3:3:6:6-Tetraphenyl-2:5-diketopiperazine (IV).—The compound (I, 3 g.) was heated on the water-bath with aqueous caustic soda (20%, 30 c.c.) for 4 hours. The solution was cooled and diluted with water to 250 c.c., when a solid was precipitated out. It was filtered, washed with water and crystallised from alcohol in colorless rectangular plates (III, 0.7 g.), m.p. 220-22°. (Found: N, 9.05. $C_{20}H_{18}ON_2$ requires N, 9.27 per cent). It is insoluble in dilute hydrochloric acid.

The alkaline filtrate, described above, was acidified with hydrochloric acid, and the solution was concentrated and cooled, when a crystalline solid was obtained which was purified by trituration with aqueous sodium bicarbonate and was recrystallised from dilute alcohol in colorless plates (IV, 0.8 g.), m.p. 242° (decomp.). It was dried at 120°-125° *in vacuo* and then analysed. (Found: C, 80.57; H, 5.68; N, 6.48; M.W., 424. $C_{28}H_{22}O_2N_2$ requires C, 80.38; H, 5.26; N, 6.69 per cent; M.W., 418). It is insoluble in aqueous sodium bicarbonate but readily soluble in cold dilute alkali and precipitated by acids. With caustic soda it gives a di-sodium derivative and the molecular weight has been determined by ascertaining the exact quantity of alkali required to form the di-sodium derivative. An aqueous solution of the substance does not give any distinctive coloration with ferric chloride. It is unaffected by heating with 25% aqueous caustic soda or by prolonged heating with concentrated hydrochloric acid. With acetic anhydride, the substance gives an alkali-insoluble diacetyl derivative, crystallising from alcohol in colorless rectangular plates, m.p. 85-86°. (Found: N, 5.52. $C_{32}H_{26}O_4N_2$ requires N, 5.57 per cent).

Action of Hydrochloric acid on compound (I): Formation of compounds (II) and (IV).—The compound (I, 5 g.) was heated under reflux with 15% hydrochloric acid (75 c.c.) for 6 hours. The mixture was cooled and the insoluble solid was filtered, washed with water and crystallised from alcohol in colorless rectangular plates (2 g.), m.p. 203-204°. Its identity with the compound (II), described previously, was confirmed by mixed m.p., a study of its properties and finally by analysis.

The above acid filtrate was concentrated and then cooled, when a crystalline solid was obtained which was recrystallised from dilute alcohol in colorless plates (1.2 g.), m.p. 242° (decomp.). Its identity with the compound (IV), described previously, was confirmed.

The author thanks Mr. Sukhamoy Bhattacharya for carrying out all the analyses recorded in this paper.

BENGAL IMMUNITY RESEARCH
INSTITUTE, CALCUTTA 16

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RESORCINOL SUCCINEIN AND ITS BROMO DERIVATIVES AS ADSORPTION INDICATORS

BY RAM CHARAN MEHROTRA

The behaviour of resorcinol succinein as an adsorption indicator in mixed halide solutions has been described. The applicability of two more dyes, dibromo- and tetrabromo- resorcinol succinein as adsorption indicators has been investigated. They have been found to be very suitable indicators for the titration of bromide, iodide and thiocyanate ions.

In a recent communication (this *Journal*, 1947, 24, 166), the applicability of resorcinol succinein as adsorption indicator to the argentometric titration of halide ions has been described. The present communication describes the use of resorcinol succinein as adsorption indicator in the mixed halide solutions and also of the dibromo and tetrabromo derivatives of the dye in argentometric titrations.

EXPERIMENTAL

Preparation of the Dyes.—The resorcinol succinein was prepared by the method recently described by Sheshadri and co-workers (*Proc. Ind. Acad. Sci.*, 1947, 26A, 99). The resorcinol succinein thus prepared had a melting point of 256°. The dye employed in the investigations previously published (*loc. cit.*) was prepared by the method of Biggs and Pope (*J. Chem. Soc.*, 1923, 123, 2934) and had the melting point 234°. However, on the repetition of the work with the purer dye, no detectable difference was found from the data already published. It appears that the slight impurities present in the resorcinol succinein by the method of Biggs and Pope are not of such a nature as to affect the adsorbability of the dye on the silver halide particles.

Dibromo and tetrabromo derivatives of the dye were prepared by the bromination of the succinein in glacial acetic acid (Sheshadri *et al.*, *loc. cit.*). The recrystallised dibromo derivative had the melting point 246° and the tetrabromo product decomposed above 300°.

0.2% Solutions of these dyes were prepared in 50% alcohol and these solutions were used as indicators throughout these investigations.

Resorcinol succinein as Adsorption Indicator.—It has been described that using resorcinol succinein as adsorption indicator, chloride ions can be titrated satisfactorily up to a dilution of $N/50$; in the case of thiocyanate ions, the indicator marks the end-point sharply up to a dilution of $N/100$, in the case of bromide, up to a dilution of $N/200$, and in the case of iodide ions, solutions as dilute as $N/4000$ may be titrated within 0.5% accuracy. It was considered of interest to study the behaviour of the indicator in mixed halide solutions.

Belladen and Piazza (*Ann. Chim. Appl.*, 1932, **22**, 631) find that although Brilliant Archill C and Chromotrope F4B are suitable indicators for all the chloride, bromide and iodide ions separately, yet when a mixture of iodide and chloride ions is titrated against silver ions, the end-point (pink→grey green) occurs, when silver nitrate equivalent to only the iodide ions present has been added. Resorcinol succinein is also quite suitable an indicator for all the three halide ions; yet in contrast to the above indicators, it resembles the ordinary indicator fluorescein in marking the end-point when the total of all the halide ions present has been precipitated.

However, the useful range of the indicator can be increased in mixed halide solutions. Chloride and bromide ions alone do not give sharp end-points when they are present in dilutions greater than $N/50$ and $N/200$ respectively. As the following tables will show, in the presence of iodide ions the chloride and bromide ions can be titrated with very sharp end-points up to dilutions of $N/200$ and $N/500$ respectively.

TABLE I

Vol. and conc. of halide soln.	Drop of indicator.	Vol. and conc. of AgNO_3 soln.	Transition of colour.	Remarks.
10 c.c. of $N/200$ -KCl+10 c.c. of $N/200$ -KI	2	20.05 c.c. of $N/200$ - AgNO_3	Light pink susp.→ deep pink ppt.	The coagulation occurs just at the end-point with the transference of light pink colour from the suspension to a deep pink colour on ppt.
10 c.c. of $N/500$ -KBr+10 c.c. of $N/500$ -KI	2	20.02 c.c. of $N/500$ - AgNO_3	Yellow susp.→ pink susp.	The colour change occurs sharply in the suspension phase, followed by coagulation occurring in a few seconds when pink coloured ppt. separates. Quite reversible to both KBr and KI.
10 c.c. of $N/100$ -KCl+10 c.c. of $N/100$ -KBr	1	20.05 c.c. of $N/100$ - AgNO_3	Pale yellow susp.→ pink susp.	Very sharp end-point. Quite sharp with respect to both KCl or KBr.
5 c.c. of $N/100$ -KI+5 c.c. of $N/100$ -KCNS	1	10 to 10.02 c.c. of $N/100$ - AgNO_3	Yellow susp.→ pink susp.	Sharp colour change in the homogeneous phase. Reversible to both potassium iodide as well as thiocyanate.

Dibromoresorcinol succinein as Adsorption Indicator.—Like the corresponding dyes from phthalic acid, dibromo derivative shows greater adsorbability than the resorcinol succinein itself. The greater adsorbability of the dye renders it unsuitable for the titration of chloride ions either in the neutral or acidic media. It, however, gives very sharp end-points in the case of bromide, thiocyanate and iodide ions and with its aid titrations are possible in acidic media, whereas the resorcinol succinein does not mark the end point in media of p_H lower than 7. However, none of the halide ions mark the end-point in the ammoniacal medium, and when mixtures of iodide and chloride ions are titrated, the end-point occurs when the total of the halide ions present has been precipitated and not at the point when only the iodide ions present have been titrated.

TABLE II

Vol. and conc. of halide soln.	Drops of indicator	Vol. and conc. of AgNO_3 soln.	Transition of colour.	Remarks.
10 c.c. of $N/10\text{-KCl}$	2	10 to 10.02 c.c. of $N/10\text{-AgNO}_3$	Orange susp. \rightarrow pink ppt.	Coagulation occurs at the end-point with the transference of colour from the suspension to ppt. However, the change of colour is not at all marked. If the chloride solution is acidified, the coagulation and adsorption of the colour on ppt. occur much before the equivalent point.
10 c.c. of $N/10\text{-KBr}$	2	"	Pale orange susp. \rightarrow pink ppt.	Coagulation just at the equivalent point with the transference of and a sharp change in the shade of colour. The end-point is sharp and reversible.
10 c.c. of $N/10\text{-KBr} + 4$ c.c. of $N\text{-HAc}$.	2	"	Yellow susp. \rightarrow pink ppt.	The end-point is sharp. The coagulation occurs with half a drop more of silver nitrate.
10 c.c. of $N/10\text{-KI}$	3	"	Yellow susp. \rightarrow pink ppt.	The coagulation occurs just a little before the equivalent point. The colour change occurs on the coagulated particles and is quite reversible. Titration is possible in presence of acetic acid. The end-point does not appear in ammoniacal solution.
10 c.c. of $N/10\text{-KCNS}$	2	9.98 to 10.02 c.c. of $N/10\text{-AgNO}_3$	Orange susp. \rightarrow deep pink ppt.	Coagulation occurs much earlier and the particles take up a slight pinkish tinge; at the equivalent point, a sharp colour change occurs with the transference of colour from the suspension to the ppt. The titration is possible in acidic solutions.

Tetrabromoresorcinol succinein as Adsorption Indicator.—Tetrabromo derivative of resorcinol succinein shows even a greater adsorbability than the dibromo derivative. However, on account of the loading in the molecule, the colour changes occurring at adsorption and desorption are not so sharp as in the case of non-brominated dye or its dibromo derivative. With the help of the dye, titration of bromide, iodide and thiocyanate ions can be carried out in neutral or acidic media. Iodide ions alone can be titrated in ammoniacal medium also and in the presence of dilute ammonia or ammonium carbonate; iodide ions alone can be titrated in the presence of chloride ions, when the chloride ions present are less than half the concentration of the iodide ions.

TABLE III

Vol. and conc. of halide soln.	Drops of indicator.	Vol. and conc. of AgNO_3 soln.	Transition of colour.	Remarks.
5 c.c. of $N/10\text{-KI}$	2	4.98 to 5.01 c.c. of $N/10\text{-AgNO}_3$	Pink susp. \rightarrow pink ppt.	Coagulation begins quite early, but the particles remain yellow. The titration is quite reversible.
5 c.c. of $N/10\text{-KI} + 3$ to 4 c.c. of $N\text{-HAc}$.	3	5 to 5.02 c.c. of $N/10\text{-AgNO}_3$	Yellow susp. \rightarrow pink ppt.	The end-point is very sharp and quite reversible. The coagulation occurs just at the equivalent point.

TABLE III (contd.)

5 c.c. of N/10-KI+0.1g. of $(\text{NH}_4)_2\text{CO}_3$	2	4.98 to 5.0 c.c. of N/10- AgNO_3	Yellow ppt. \rightarrow pink ppt.	The coagulation begins from the beginning, but the particles remain yellow. About 0.5% before the equivalent point, the particles assume a pinkish shade, but the suspension becomes clear just at the equivalent point with deepening of colour on the particles.
Above+2.5 c.c. N/10-KCl	2	"	"	"
5 c.c. of N/10-KBr	2	5 to 5.02 c.c. of N/10- AgNO_3	Pink susp. \rightarrow pink ppt.	The colour change at the end-point is not marked; the colour is merely transferred from suspension to the precipitate.
5 c.c. of N/10-KBr+2 c.c. of N-HAc	3	5 to 5.01 c.c. of N/10- AgNO_3	White susp. \rightarrow pink ppt.	Cogulation occurs just at the end-point. The end-point is very sharp.
5 c.c. of N/10-KCNS	2	4.98 to 5 c.c. of N/10- AgNO_3	Orange susp \rightarrow pink ppt.	Coagulation much earlier; particles take up slight colour before the end-point. The end-point is much sharper in the presence of acetic acid, in which case, the particles remain colorless up to the end-point.
5 c.c. of N/10-KI+2.5 c.c. of N/10-KCl+0.1g. $(\text{NH}_4)_2\text{CO}_3$ or 1 c.c. of N- NH_4OH	2	4.98 to 5.0 c.c. of N/10- AgNO_3	Yellow ppt. \rightarrow pink ppt.	The coagulation begins quite early, but the particles remain yellow.
5 c.c. of N/10-KCl				The adsorption of the dye and the colour change occurs much before the end-point. The titration is not possible in neutral or acidic medium.

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CHEMICAL LABORATORIES,
THE UNIVERSITY, ALLAHABAD.

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DYES DERIVED FROM SUCCINIC AND MALEIC ACID AND THEIR DERIVATIVES AS ADSORPTION INDICATORS

By RAM CHARAN MEHROTRA

A comparative study has been made between the applicability of dyes obtained from succinic and derived succinic acids and the corresponding dyes from maleic acids as adsorption indicators in argentometric titrations. It has been shown that whereas succinic acid derivatives—resorcinol succinein and itaconein—serve as very useful indicators, the corresponding dyes from maleic acid do not have any applicability. The behaviour has been explained on the existing theories of colour and of adsorption indicators. As a result of the investigation, a new adsorption indicator, resorcinol itaconein, has been described.

Since the discovery of Fajans (*Z. Electrochem.*, 1923, 29, 495), an extensive study has been made of the dyes derived from phthalic acid, *o*-sulphobenzoic acid and a few other dyes as adsorption indicators in argentometric titrations. No attempt seems to have been made to make a systematic study of the suitability of the corresponding dyes derived from the other dibasic acids as adsorption indicators. In recent communications from these laboratories, the applicability of the dyes derived from succinic acid (Mehrotra, Tewari and Dube, *J. Indian Chem. Soc.*, 1947, 24, 165), quinolinic and cinchomeric acids (Mehrotra, *Proc. Nat. Acad. Sci., India*, 1946, 16, 148) has been described. It has been shown that resorcinol succinein is a very suitable indicator for the argentometric titrations of chloride, bromide and iodide ions and in certain cases, it works even better than the classical adsorption indicator, fluorescein. It was considered of interest to try the applicability of maleic acid derivatives as adsorption indicator and to compare the applicability of resorcinol malein with that of the succinein. On finding the inapplicability of resorcinol malein as adsorption indicator in argentometric titrations, the comparison has been extended to two isomeric dyes, resorcinol itaconein (methylene-succinein) and resorcinol citraconein (methyl-malein) and similar results have been obtained in their case also.

EXPERIMENTAL

Preparation of the Dyes.—Resorcinol succinein and malein were prepared as described by Sheshadri and co-workers (*Proc. Ind. Acad. Sci.*, 1947, 26A, 308).

Resorcinol itaconein and citraconein were prepared by the method of Dhar and Dutt (*J. Indian Chem. Soc.*, 1927, 4, 247, 253).

Resorcinol malein as Adsorption Indicator.—A 0.2% solution of the dye was prepared in alcohol and used as adsorption indicator in this investigation.

When the chloride solution (about *N*/10) is titrated against silver ions, the coagulation of the silver chloride occurs a little before the equivalent point and the dye is adsorbed on the precipitate. However, the colour developed on the particles due to the adsorption of the dye is not bright and does not differ markedly from the colour of the dye in suspension, and hence the end-point is not sharp.

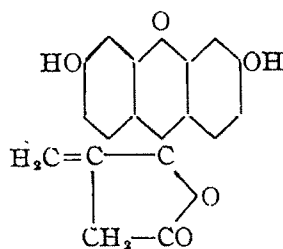
In the case of thiocyanate ions, the coagulation of the precipitate begins quite early and at the equivalent point, the particles adsorb the dye with the development a slight pink colour. The colour developed both in the case of the chloride and the

thiocyanate is much less intense than in the case when succinein is used in the place of malein as indicator.

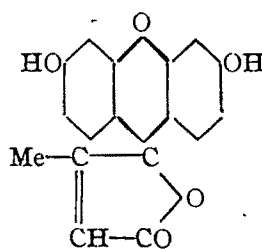
In the case of bromide and iodide ions, a very sharp and well defined colour change of yellow to pink has been described to occur when resorcinol succinein is used as an adsorption indicator. However, when resorcinol malein is used as indicator in place of the succinein, no perceptible colour change occurs on the coagulated particles.

Resorcinol Itaconein and Citraconein as Adsorption Indicators

Resorcinol itaconein and resorcinol citraconein are two isomeric dyes having the following constitutions :



Resorcinol itaconein.



Resorcinol citraconein.

The itaconein may be said to be a derivative of succinic acid, whereas the citraconein is a derivative of the maleic acid. It is of interest to observe that similar to the comparative behaviour of resorcinol succinein and malein as adsorption indicators, itaconein gives very sharp end-points and is a very suitable indicator for the argentometric titration of the chloride, bromide, iodide and thiocyanate ions, whereas the citraconein does not give sharp end-points in the titration of halide ions.

Titration of Chloride Ions against Silver Ions.—When chloride ions are titrated against silver nitrate using resorcinol itaconein (0.2% solution) as indicator, a very sharp colour change, colorless to pink, occurs at the equivalent point. When the solutions have a concentration of about $N/10$, the coagulation occurs before the end-point, but the particles remain white so long as the chloride ions are present in excess in the supernatant liquid, and develop a bright pink colour as soon as the silver ions become in slight excess. In the case of dilute solutions (about $N/100$), the coagulation of the silver chloride does not occur and a sharp colour change (light pink to deep pink) occurs in the suspension phase itself. With resorcinol itaconein as adsorption indicator, the chloride ions can be titrated with very sharp end-points up to a dilution of $N/100$.

The colour change is not at all sharp, when in the above titration resorcinol citraconein (0.2% solution in alcohol) is used as an adsorption indicator in the place of the itaconein. In the more concentrated solutions, the colour developed on the particles is much less in intensity than in the case of the itaconein. In the case of dilute solutions (about $N/100$), coagulation of the silver chloride does not occur, but there is no sharp colour change at any stage. The colour of the suspension goes on becoming

more and more pink as the silver nitrate solution is run in, but there no perceptible colour change occurring sharply at any stage.

Titration of Thiocyanate Ions.—When the thiocyanate ions (about $N/10$) are titrated against silver nitrate (about $N/10$) solution, using resorcinol itaconein as adsorption indicator, coagulation of the silver thiocyanate begins quite early, but the particles remain colorless so long as the thiocyanate ions are present in excess and assume a bright pink colour just at the equivalent point. The titrations can be carried out up to a dilution of $N/200$ with very sharp end-points; in the more dilute solutions the colour change (colorless to pink) occurs in the apparently homogeneous suspension phase.

In the case when resorcinol citraconein is used as the indicator in place of the itaconein, the colour developed on the particles is much lighter and so the end-point is much less sharp.

Titrations of Bromide and Iodide Ions.—Using resorcinol itaconein as adsorption indicator, bromide and iodide ions can be titrated with very sharp and well defined end-points. In the case of the bromide ions the colour change at the end-point is from colorless or pale yellow to bright pink and very sharp end-points are obtained up to a dilution of $N/250$. The colour change in the case of iodide ions is from yellow to bright pink and titrations are possible up to a dilution of $N/500$ solutions.

When citraconein is used as adsorption indicator, the colour change is not at all sharp in the case of bromide ions. However, in the case of iodide ions the end-point is sufficiently sharp and the colour change occurs from yellow to pink, though the pink shade developed in the case of citraconein is much less bright than in the case of itaconein under identical conditions. Using citraconein as indicator, the colour change at the end-point is not sharp in dilutions greater than $N/100$.

The following table records a few of the results of the titrations carried out with the help of a microburette using a 0.2% solution of resorcinol itaconein as adsorption indicator.

TABLE I

Conc. of halide soln. (5 c.c.)	Drops of Indicator.	Conc. of AgNO_3 soln.	Transition of colour.	Remarks.
$N/10\text{-KCl}$	2	5 to 5.02 c.c. of $N/10\text{-AgNO}_3$	White ppt. \rightarrow pink ppt.	The coagulation of the silver chloride particles begins much earlier. The colour change though occurring on coagulated particles is very sharp and quite reversible.
$N/100\text{-KCl}$	2	„	Light pink susp. \rightarrow deep pink susp.	The coagulation of the ppt. does not occur. The colour change occurs in the apparently homogeneous phase and is quite reversible.
$N/10\text{-KBr}$	2	4.99 to 5 or c.c. of $N/10\text{-AgNO}_3$	Pale yellow ppt \rightarrow pink ppt.	The end-point is very sharp and quite reversible.
$N/250\text{-KBr}$	2	5 to 5.02 c.c. of $N/250\text{-AgNO}_3$	White susp. \rightarrow pink susp.	The end-point is very sharp. The coagulation of the ppt. occurs a few seconds afterwards and the ppt. is pink coloured, changing to black very rapidly.
$N/10\text{-KI}$	2	„	Yellow ppt. \rightarrow pink ppt.	Very very sharp end-point. Colour change reversible.
$N/500\text{-KI}$	2	5 to 5.03 c.c. of $N/500\text{-AgNO}_3$	Yellow susp. \rightarrow pink susp.	No coagulation. The colour change occurs in the apparently homogeneous phase.

DISCUSSION

It is of interest to observe as the above investigation demonstrates that whereas resorcinol derivatives of succinic acids and acids derived from it serve as very suitable adsorption indicators, the corresponding dyes derived from maleic acid do not show any sharp colour change on the particles. In a number of communications, Dutt and Thorpe (*J. Chem. Soc.*, 1925, 2524), Tewari and Dutt (*J. Indian Chem. Soc.*, 1928, 5, 60) and Dhar and Dutt (*ibid.*, 1927, 4, 247, 253) have shown that the dyes derived from maleic acid and its derivatives have a deeper colour than the corresponding dyes from succinic acid. This increment in absorption, they have explained to be due to the introduction of double bond which hinders free rotation in the molecule. Fajans and Hassel (*loc. cit.*) have explained the colour change occurring in the adsorption indicators to be due to the deformation of the electron shell that the dye ions undergo when they are in the force fields of oppositely charged and neighbouring ions. This deformability may be expected to be less in the dyes with a double bond than with the dyes having no double bond and hence no restricted rotation. The simple qualitative explanation explains very easily the observed marked difference between the dyes derived from succinic and maleic acids.

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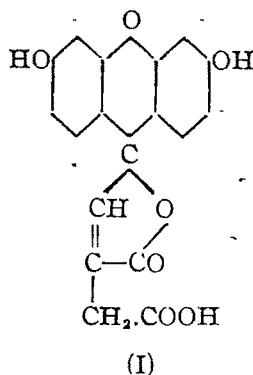
Received June 8, 1948.

RESORCINOL ACONITEIN AND TRICARBALLYLEIN AS ADSORPTION INDICATORS IN ARGENTOMETRIC TITRATIONS

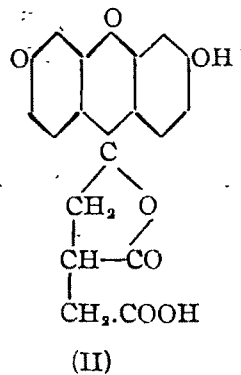
BY RAM CHARAN MEHROTRA

In a comparative study of the behaviour of resorcinol aconitein and tricarballeylein as adsorption indicators in argentometric titrations, it has been observed that whereas the latter is a very suitable indicator for the purpose, the former does not develop any distinct colour on being adsorbed on the silver halide bodies. The observed difference has been explained in a simple manner and casually confirms the structure assigned to the aconitein by the previous workers. As a result of the investigation, a very sensitive indicator for the titration of halide and thiocyanate ions against silver ions has been described.

In a recent communication from these laboratories (Mehrotra, this *Journal*, 1948, 25, 523, it has been shown that whereas dyes derived from succinic acid-resorcinol succinein and itaconein serve as very suitable indicators for the titrations of halide ions against silver ions, the corresponding dyes from maleic acid-resorcinol malein and citraconein are not at all suitable for the purpose. The difference in the behaviour of the two classes of dyes has been explained on the basis of restricted rotation due to a double bond in the maleic acid derivatives. It was considered of interest to extend the study to the comparative behaviour of resorcinol aconitein and tricarballeylein. Resorcinol aconitein and tricarballeylein have the structure (I) and (II) shown below:

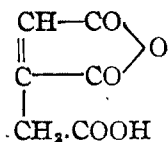


Resorcinol aconitein

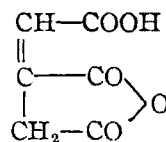


Resorcinol tricarballeylein.

Aconitic anhydride could theoretically have either of the structures (III) or (IV), but the former is the more stable of the two because the interposition of a double bond between the two carbon atoms brings the two carboxylic groups so near to each other that the anhydride formation between them takes place with the greatest ease (Beasley, Ingold and Thorpe, *J. Chem. Soc.*, 1915, 107, 1080; Ingold and Thorpe, *ibid.*, 1919, 115, 320; Kon, *ibid.*, 1921, 119, 810; Dhar and Dutt, *J. Indian Chem. Soc.*, 1927, 4, 253).



(III)



(IV)

Dikshit and Tewari (*J. Chem. Soc.*, 1931, 2511) have arrived at similar conclusions from a study of the dyes derived from the two acids. It is of interest to observe that the comparative behaviour of the resorcinol dyes of these acids as adsorption indicators is in agreement with the structures proposed above. Like the derivatives of maleic acid-resorcinol malein and citraconein, resorcinol aconitein also is not a suitable adsorption indicator for the argentometric titrations, whereas the corresponding succinic acid derivative, resorcinol tricarballeyein marks the end-points very sharply in the titrations of halide ions against silver ions.

EXPERIMENTAL

The dyes, resorcinol aconitein and tricarballeyein, were prepared according to the method described by Dikshit and Tewari (*loc. cit.*). 0.1% Solutions of the dyes were prepared in alcohol and these solutions (generally one drop for each 5 c.c. of the halide solution to be titrated) were employed as adsorption indicators throughout the following investigations.

Titration of Chloride Ions against Silver Ions.—When a chloride solution (about $N/10$) is taken in a beaker and a drop of resorcinol tricarballeyein is added to it, the solution shows a brilliant green fluorescence. As the silver nitrate solution (about $N/10$) is gradually added to it, the solution becomes yellow. Coagulation of the silver chloride begins quite early and the particles take up a slight pinkish shade. Just at the equivalent point, with half a drop of the silver nitrate solution, the precipitate as well as the supernatant suspension takes up a very bright pink shade. The colour on the particles becomes much lighter when a few drops of acetic acid ($N/10$) is added to the washed pink precipitate; the colour on the particles disappears also with the addition of ammonia to the precipitate with the appearance of a bright green fluorescence in the supernatant solution. When the titrating solutions have a concentration of about ($N/100$), the colour change (pinkish yellow to bright pink) occurs in the suspension phase. The colour change is quite reversible; even in the more concentrated solutions, though the colour change occurs on the coagulated particles, yet the colour change is so reversible that the titration can be carried out accurately even in the opposite direction.

However, when resorcinol aconitein is used as indicator instead of the tricarballeyein, the pink colour developed on the particles on the adsorption of the dye at the equivalent point is much lighter in shade and the end-point is not at all sharp. The chloride solution with a few drops of the indicator added to it has a light yellow colour and takes up a light orange colour as a little silver nitrate solution is run in. The co-

agulation of the precipitate begins quite early, but the particles remain almost colorless and become light pink at the equivalent point (about 0.6% excess of silver nitrate is required).

Titration of Thiocyanate Ions against Silver Ions.—When the solutions having a concentration of about ($N/10$) are titrated using resorcinol tricarballeyein as adsorption indicator, the coagulation of the precipitate begins quite early, but just at the equivalent point the bright yellow colour of the suspension is discharged with a simultaneous development of a bright pink colour on the particles of the coagulated precipitate which remains white in shade before the end-point. The above colour change, though occurring on the particles of the coagulated precipitate, is very sharp and quite reversible. In the case the solutions are dilute (about $N/200$), a very sensitive colour change from yellow to pink occurs in the apparently homogeneous suspension phase.

However, as in the case of the chloride, the end-point is not so sharp and the pink shade developed on the particles is much lighter when resorcinol aconitein is used as indicator instead of the tricarballeyein.

Titration of the Bromide Ions against Silver Ions.—Using resorcinol tricarballeyein as adsorption indicator, a very sharp colour change from yellow to bright pink occurs at the equivalent point. The colour change occurs on the particles of the coagulated precipitate in the case of the concentrated solutions, but in the suspension phase, when the titrating solutions are dilute. The titration with sharp end-points is possible when the solutions have a dilution up to about $N/500$. The colour change is quite reversible and the titration is possible in the reverse order with the colour change occurring in the opposite manner.

The end-point are not at all sharp using resorcinol aconitein as adsorption indicator. The colour developed on the particles on the adsorption of the dye is very light and quite indistinct.

Titration of Iodide Ions against Silver Ions.—When a iodide solution is titrated against silver nitrate solution using resorcinol tricarballeyein as adsorption indicator, a very sharp and quite reversible colour change from yellow to bright pink occurs. When the solutions are relatively concentrated, then the coagulation of the precipitate occurs almost simultaneously with the adsorption of the dye at the equivalent point. In the case of dilute solutions, the suspension retains a bright green fluorescence up to the end-point and at the equivalent point, half a drop of the silver nitrate solution inhibits the fluorescence and makes the suspension pink. The end-point is quite sharp even when the titrating solutions are as dilute as $N/1000$.

In the case when resorcinol aconitein is used as adsorption indicator, similar colour changes take place and the end-point is easily detectable, but the colour developed on the particles or in the suspension phase is much lighter. Solutions can be titrated upto a dilution of $N/500$.

The following table records a few of the experimental results obtained using resorcinol tricarballeyein as adsorption indicator :

TABLE I

Conc. of halide soln. (5 c.c. taken).	Drops of Indicator.	AgNO ₃ soln.	Transition of colour	Remarks.
N/10-KCl	2	4.99 to 5.01 c.c., of N/10	Yellow susp. → pink ppt.	The end-point is very sharp and quite reversible. The titration is possible in the opposite direction.
N/100-KCl	2	5 to 5.02 c.c. of N/100	Pink-yellow susp. → pink susp.	"
N/10-KCNS	2	5.00 c.c. of N/10	White ppt. → pink ppt.	The coagulation of the ppt occurs very early. The colour change is very sharp and reversible.
N/200-KCNS	2	5.02 c.c. of N/200	Yellow susp. → pink susp.	The silver thiocyanate does not coagulate at all. The end-point is very sharp and reversible.
N/500-KBr	1	5.02 to 5.03 c.c. of N/500	Yellow susp. → pink susp.	End-point is quite sharp and occurs in the apparently homogeneous phase. The titration is possible in opposite direction.
N/100-KI.	2	5 to 5.02 c.c. of N/10	Yellow susp. → pink ppt.	The coagulation occurs just at the end-point with the transference of the yellow colour of the suspension to a bright pink colour on ppt.
N/1000-KI	1	5 to 5.02 c.c. of N/1000	Greenish yellow susp. → pinkish yellow susp.	The solution has a bright green fluorescence right up to the end-point. Just at the end-point, the fluorescence ceases, being replaced by a pinkish tinge.

DISCUSSION

As has been shown in the earlier communication (*loc. cit.*), the deformability of the electronic orbits and consequently the development of colour on adsorption is much inhibited when a double bond is present at an active spot in the dye molecule. The reasoning put forward by Thorpe and co-workers in favour of the structure (III) as the one representing the aconitein can be applied for explaining the cause of a much lesser development of colour in the case of the aconitein than in the case of tricarballeyein. The presence of the double bond make the anhydride formation much easier in the case of the maleic acid derivatives and hence the opening of this anhydride ring which requires a greater force and strain in the case of maleic acid derivatives than in the corresponding succinic acid derivatives. This lessening of the ease with which the anhydride ring can be opened will have an effect in inhibiting the tautomeric change producing the quinonoid structure, as it requires the opening of the said ring and hence the colour will be much less pronounced in the case of maleic acid derivatives than in the corresponding succinic acid derivatives. The observed difference in the behaviour of the resorcinol aconitein and tricarballeyein is thus simply explained.

The author wishes to thank Dr. J. D. Tewari for his kind help in the preparation of the indicator dyes.

STUDIES ON GUM JEOL (*LANNEA GRANDIS*, ENGLER). PART VI.
INFLUENCE OF NEUTRAL SALTS ON SOME ELECTRO-
CHEMICAL AND VISCOUS PROPERTIES

By S. N. MUKHERJEE AND (MISS) K. K. ROHATGI

Influence of neutral salts with cations and anions of different valencies on the p_H , specific conductance and relative viscosity of gum jeol solutions have been examined. Both cations and anions show a tendency towards an increase of p_H at low concentrations followed by a marked depression at higher concentrations. Specific conductance does not show any point of special interest, while relative viscosity shows peculiar variations with ions having different valencies.

Conclusions arrived at from the study of the influence of concentration of the gum jeol solution on the different physical and electrochemical properties thereof (Part V of this series, this *Journal*, 1948, 25, 339) go to show that a gum solution should be treated as composed of particles which are colloidal micelles surrounded by a double layer of counter ions rather than polyvalent ions under the influence of the ionic atmosphere.

The work embodied in the present paper is an extension of the above with a view to further examination of the above conclusions from an altogether different direction, viz, by noting the changes produced in some of the electrochemical and viscous properties under the influence of neutral salts having cations and anions with different valencies. The changes in hydrogen ion activity and specific conductance have been the main targets of attack, as these are expected to show evidences of cation or anion exchange, if any, produced by neutral salts as in many colloidal systems having particles with large surfaces (cf. the extensive works done in this direction by Mukherjee and co-workers,). The changes in the viscous properties have also been examined as they might be of interest to the industrial use of this gum where the viscous properties of the gum solution have been of considerable importance.

For this reason chlorides of Na, K, Ba and Al and the potassium salts of the anionic radicals Cl, NO₃, SO₄, ferri- and ferrocyanides were tried.

EXPERIMENTAL

The methods for the preparation of the solution as well as those for measurements of p_H , specific conductance and relative viscosity have been the same as described in Part V (*loc. cit.*) of this series. Temperature at which these measurements were carried out was the room temperature (30°). The viscometer was of the Ostwald type and showed the time of flow for water to be about 60 seconds. Reproducibility of measurements was the same as mentioned in Part V (*loc. cit.*).

Only freshly prepared gum solutions were used in these investigations. It has been observed that solutions of this gum keep well and do not show any signs of change in their p_H , specific conductance or relative viscosity up to about 40 days after preparation of the aqueous solution, beyond which the solutions have been observed to show signs

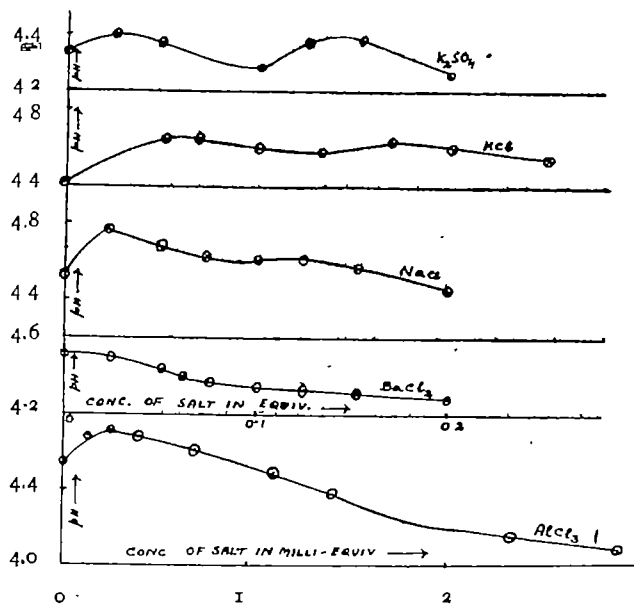
of deterioration.* In the present investigation a gum solution, older than 30 days, was never used.

In the following the effect of neutral salts on the p_H was studied with one preparation (A) and that on conductance and relative viscosity with another (B), both having the identical concentration. The data on relative viscosity are the mean of five or six determinations of the time of flow which seldom differed from each other by more than 1 to 2 seconds. The density determination was, however, made only once for each concentration of the neutral salts.

The salts used were of Merck's reagent or B.D.H. 'Analar' quality. Solutions were always prepared in equilibrium water having specific conductance of 2.0×10^{-6} mho at 30° . Results appear below.

Hydrogen-ion Activity.—Cationic influence was studied with the help of NaCl, BaCl₂ and AlCl₃ with a gum solution whose initial p_H was 4.5 (conc., 0.5 g. per 100 c.c. of solution). Results, represented graphically in Fig. 1, show that with NaCl and AlCl₃ there is an initial rise of p_H followed by a subsequent decrease at high salt concentrations. The decrease of p_H with NaCl is much smaller than with AlCl₃, where hydrolysis of the salt into HCl is probably responsible for a more marked diminution of p_H . The initial rise, although small, is significant. KCl and K₂SO₄ all show this increase (vide Fig. 1), which marks a slight departure from what is commonly observed in those cases where H-ion exchange is known to occur and where p_H tends to diminish right from low concentrations. The divalent Ba-ion (in BaCl₂) does not, however, show this increase. The p_H remains almost constant over a certain range of concentrations at the

FIG. 1



* This aspect will be taken up in a future communication (Part VIII).

beginning beyond which there is a steady downward course. Comparing the depression of p_H at higher concentrations, the cationic order appears to run as $Al : > Ba > Na, K$. With Al ion, where the hydrolysis of the salt is probably responsible for the more marked changes, as observed herein, the effects occur at much lower concentrations than in Ba, Na and K .

The anionic influence has been observed with KCl and K_2SO_4 (i.e., mono and divalent anions) only. The curves show a second rise of p_H at still higher concentrations with these salts as well as with $NaCl$. With $NaCl$ and KCl this was small but with K_2SO_4 it was more marked, being of the magnitude of about 0.2 p_H units. $BaCl_2$ and $AlCl_3$ do not show this second rise. With monovalent anion this is small but it increases with increase in the valency of the anion. Possibly with $BaCl_2$ and $AlCl_3$ the effect of the Cl -ion is masked by a stronger effect of cations of higher valencies. Anions of higher valencies could not be examined for practical inconvenience.

The p_H (or H -ion activity) is thus affected in a peculiar manner by cations and anions of different valencies. To understand the nature of these variations (cf. Fig. 1) it appears essential to assess the rôle of two important influencing factors, one of which being the change of ionic strength on addition of neutral salts which tends to diminish the activity of the ions. An initial rise of p_H with Na and Al ions probably owes its origin to this factor. The second influencing factor is the base exchange capacity of the cations which as a rule tends to diminish p_H . The mutual balance of these two opposing factors appears ultimately to determine the nature of the overall change in p_H of the solution in presence of neutral salts. The initial rise of p_H with $NaCl$ and $AlCl_3$ may be the result of the change in ionic strength. It is a common experience that base exchange capacity of divalent ions is higher than that of monovalent ones. The absence of an initial rise of p_H at low concentrations of $BaCl_2$ might thus be due to a stronger base exchange capacity of the Ba ions. The case of Al ions is complicated by partial hydrolysis of the salt.

The rise of p_H at higher concentrations of KCl and K_2SO_4 , which has already been referred to as the anionic effect on p_H , appears to find a qualitative explanation if we attribute them to the effect of higher ionic strength at higher salt concentrations. Comparing KCl with K_2SO_4 we find that K_2SO_4 having a divalent anion will increase the ionic strength much more rapidly with concentration and will show the effect thereof earlier than KCl . The occurrence of the maximum at lower concentrations of K_2SO_4 than with KCl thus corroborates these conclusions, at least partially.

Specific Conductance.—Observations have been presented in Table I and graphically shown in Figs. 2 and 3. In these measurements the concentration of the gum was kept constant, while that of the salt only varied by taking 5 c.c. of the gum solution and mixing with it exactly 15 c.c. of mixtures of water and the electrolytic solution in different proportions, so that the final volume was 20 c.c. in all. The gum solution thus became exactly 4 times diluted. Readings were taken in ten minutes' time after mixing the salt solution with the solution of the gum.

TABLE I

Sp. conductance of gum solution at 4 times dilution = 1.882×10^{-4} mho.

Initial conc. = 0.489%. Temp. = 30°.

Salt.	Conc.	Sp. cond. of the salt soln.	Sp. cond. of mix. (calc.)	Sp. cond. (obs.)	Difference
KCl	0.02 N	0.0037	0.0039	0.0036	8.333%
	0.04	0.0054	0.0056	0.0052	7.691
	0.07	0.0084	0.0086	0.0086	0.0
	0.11	0.0135	0.0137	0.0135	1.451
	0.13	0.0168	0.0170	0.0150	13.33
	0.20	0.0235	0.0237	0.0227	4.406
BaCl ₂	0.025	0.0027	0.0029	0.0025	16.0
	0.038	0.0036	0.0038	0.0036	5.555
	0.062	0.0060	0.0062	0.0056	10.720
	0.10	0.0088	0.0090	0.0087	3.448
	0.11	0.0101	0.0103	0.0097	6.186
	0.13	0.0112	0.0114	0.0101	12.870
	0.16	0.0139	0.0141	0.0135	4.445
	0.19	0.0155	0.0157	0.0144	9.026
AlCl ₃	1.439×10^{-2}	1.933×10^{-4}	3.815×10^{-4}	3.640×10^{-4}	4.807
	2.158	2.830	4.712	4.298	9.632
	3.597	4.550	6.432	5.772	11.43
	4.6767	5.872	7.754	6.848	13.23
	5.756	7.137	9.019	8.017	12.50
	6.475	7.769	9.651	8.314	16.08
KNO ₃	0.025	0.0033	0.0034	0.0033	8.031
	0.038	0.0049	0.0051	0.0046	10.86
	0.063	0.0077	0.0079	0.0076	3.948
	0.100	0.0110	0.0112	0.0106	5.661
	0.138	0.0144	0.0146	0.0131	11.45
	0.188	0.0173	0.0174	0.0172	1.162
K ₂ SO ₄	0.025	0.0037	0.0038	0.0034	14.71
	0.038	0.0055	0.0057	0.0051	11.77
	0.062	0.0086	0.0088	0.0080	10.0
	0.100	0.0127	0.0129	0.0110	17.28
	0.125	0.0157	0.0159	0.0137	16.65
	0.188	0.0219	0.0221	0.0202	9.406
K ₃ Fe(CN) ₆	0.026	0.0032	0.0034	0.0032	6.25
	0.038	0.0046	0.0048	0.0046	4.347
	0.064	0.0078	0.0079	0.0074	6.325
	0.102	0.0119	0.0121	0.0106	14.16
	0.153	0.0155	0.0157	0.0143	9.790
	0.192	0.0177	0.0179	0.0168	6.548
K ₄ Fe(CN) ₆	0.025	0.0028	0.0029	0.0023	26.06
	0.038	0.0038	0.0040	0.0032	25.0
	0.063	0.0058	0.0060	0.0048	25.0
	0.100	0.0073	0.0075	0.0071	5.633
	0.150	0.0104	0.0106	0.0101	4.951
	0.1885	0.0128	0.0130	0.0116	12.07

FIG. 2

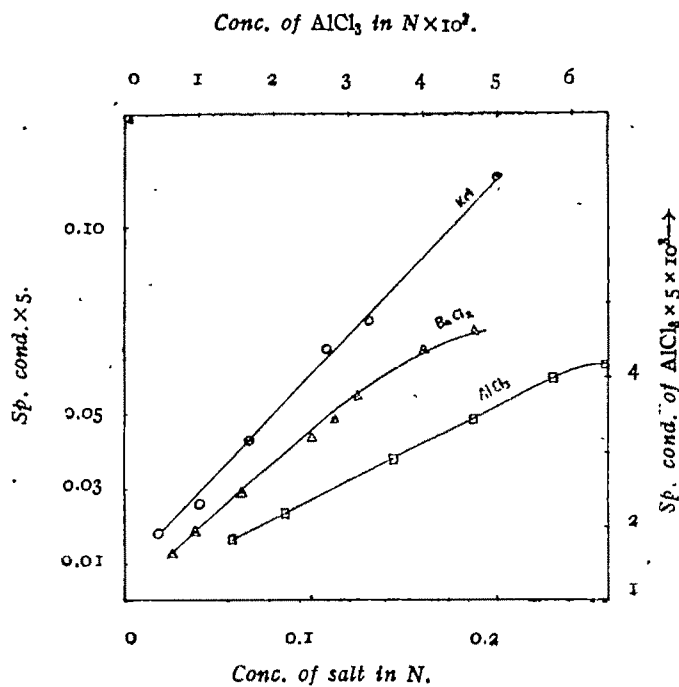
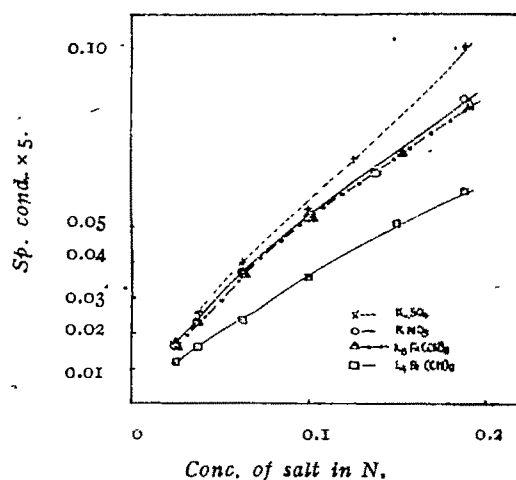


FIG. 3



The significant fact to be noted in this connection is that the observed specific conductance is never equal to the sum of those of the salt and gum solutions at corresponding concentrations. The observed values are in most cases less than the calculated values obtained by addition of specific conductance values. Both cations and anions behave alike in this respect.

The observations of Pauli and Ripper (*Kolloid Z.*, 1933, 62, 162) on specific conductance of mixtures of KCl and arabic acid solutions at different ratios of their concentrations indicate that the observed specific conductance is always higher than the calculated values. This is just the reverse of what has been observed in the present case. The percentage differences, as calculated by them, did not show any regularity with increasing concentrations of the salt which were small in their case as compared to those in the present case, the highest concentration being $2.2 \times 10^{-2}N$. They have explained the higher values of observed specific conductance as the outcome of the liberation of hydrogen ions by the addition of salts (i.e., the base exchange in presence of KCl).^{*} With this gum no such increase in hydrogen ion activity could be observed. On the other hand, both anions and cations, excepting the salt $BaCl_2$, tended to increase the p_H at small concentrations but showed variations of complicated nature at higher concentrations. Over and above this, the fact that this gum possesses some buffering properties (vide Part V) is likely to render its behaviour more complicated. A lowering of specific conductance can thus be understood in the light of the above observations. The irregular manner in which the specific conductance varies with the concentrations of the added salts, however, awaits further clarification.

Relative Viscosity.—The cationic effect on relative viscosity appears in Fig. 4. With NaCl and $BaCl_2$ there is an initial drop at low salt concentrations, this drop being

FIG. 4

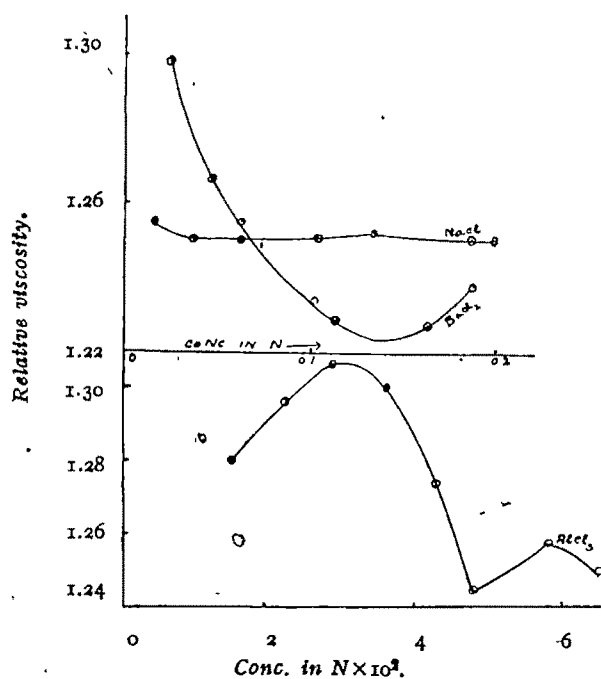
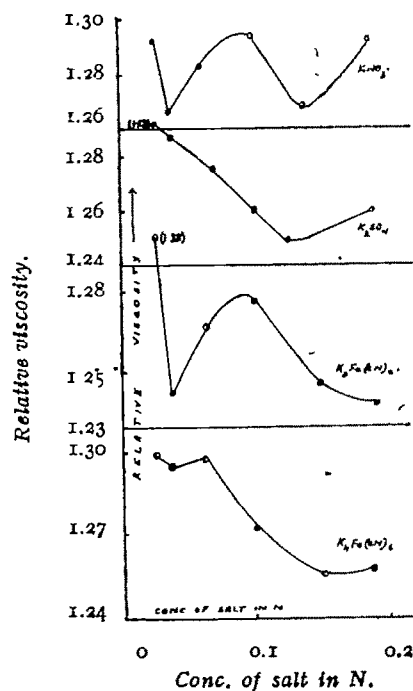


FIG. 5



* They observed a change of a_H^+ from 9.16×10^{-4} to 1.22×10^{-3} by addition of $4 \times 10^{-2}N$ -KCl to 0.42% arabic acid solution.

less marked with NaCl. With AlCl_3 , however, there was no initial drop but on the contrary a tendency to rise was evident at low concentrations. The initial decrease of viscosity has been observed by other workers working in different colloidal systems (cf. Bungenberg de Jong in yeast nucleic acid solution, *Rec. trav. chim.*, 1930, **44**, 658; Kruyt and Tendeloo in gum arabic solutions, *Koll.-Chem. Beih.*, 1929, **29**, 396).

The increase in viscosity curve (Fig. 4) with Ba and the second increase with Al ions, followed by a decrease at higher concentrations, offer points of interest. AlCl_3 has been observed to have a coagulating effect upon the gum solution and at concentrations higher than the coagulating one it has been observed to bring about a reversal of charge. BaCl_2 has been observed to possess no such coagulating effect within the concentration range used here as studied by turbidity measurements.

As to the variation of relative viscosity by Al ions (Fig. 4) it appears that the behaviour is rendered complicated by the occurrence of hydrolysis of the salt. With KCl the viscosity practically shows no change. BaCl_2 depresses this markedly with concentration. This is, however, quite the reverse of what is usually observed with those ions which show a stronger base exchange capacity. It appears therefore that in the present case, the base exchange capacity is not the only factor in determining the variation of viscosity.

Anionic effect was studied with KNO_3 , KCl, K_2SO_4 , $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ and has been graphically shown in Fig. 5. The curves for monovalent and trivalent ions show a sharp decrease of viscosity at lower concentrations followed by a rise to a maximum at higher concentrations after which there is again a tendency to decrease.

The effect of the anions is also peculiar in that the mono and tri-valent ions show a strong depression at low concentrations which may be attributed to "electroviscous effect" as proposed by Kruyt (cf. Alexander, "Colloid Chemistry", Vol. I, p. 306). The curves for divalent and tetravalent anions show a gradual diminution instead of a sharp one. The monovalent and trivalent ions further show an increase of viscosity at higher concentrations which are altogether absent in the case of bivalent and tetravalent anions.

The viscous properties thus show peculiarities which cannot be explained from our experience with other colloidal electrolytes. The viscous properties in presence of salts are again the most important ones which have been of interest in the industrial use of this gum. But further work appears necessary before any definite conclusions can be arrived at on this point and such work is in progress.

The authors' best thanks are due to Dr. H. L. Ray, Dr. Ing., the Head of the Chemical Engineering Department for his keen interest and to Dr. T. Sen, Principal for rendering all facilities in connection with this work.

SYNTHESIS OF SUBSTITUTED DINITROPHENYLKETONES AND PHENYLACETIC ACIDS. PART V

A. B. SEN AND P. M. BHARGAVA

2: 6-Dinitro-4-chlorophenyl-acetone and -acetic acid and 2-methyl-3-carbethoxy-4-amino-6-chloroindole have been prepared.

The reaction described in previous communications (Sen and Bhargava, *J. Indian Chem. Soc.*, 1947, 24, 268, 371; 1948, 25, 282, 403) has been extended to the preparation of 2: 6-dinitro-4-chlorophenyl -acetone and -acetic acid, by the condensation of mono-sodium derivative of acetoacetic ester with 2: 5-dichloro-1: 3-dinitrobenzene and subsequent hydrolysis. Similar condensation with malonic ester yields 2: 6-dinitro-4-chlorophenylmalonic ester. The reduction of 2:6-dinitro-4-chlorophenylacetoacetic ester results in the formation of an indole derivative.

EXPERIMENTAL

2:5-Dichloro-1-nitrobenzene and 2:5-Dichloro-1:3-dinitrobenzene.—The former was obtained by adding *p*-dichlorobenzene (20.8 g.) in small quantities, with stirring, to fuming nitric acid (*d* 1.52, 26 c.c.) cooled in ice-water. The product after standing at the room temperature for a short time, was poured into ice-water, and the solid that separated out was washed and dried, m.p. 54°, yield 27 g.

To obtain 2:5-dichloro-1:3-dinitrobenzene, 2:5-dichloro-1-nitrobenzene (27g.) was covered with sulphuric acid (conc., 90 c.c.), cooled in ice water, and treated with nitrating mixture (fuming nitric acid 28 c. c., *d*, 1.52 and fuming sulphuric acid 28 c.c., 26% SO₂) dropwise. When the addition of the nitrating mixture was complete, it was heated on a water-bath at 85° and stirred for 3 hours. The product was allowed to stand overnight at room temperature and poured over crushed ice; the precipitate was removed, washed and recrystallised from hot alcohol, yield 28 g.

2:6-Dinitro-4-chlorophenylacetoacetic Ester—Acetoacetic ester (18 g.) was treated with sodium (3.2 g.) in anhydrous ether; after the last traces of sodium had disappeared, the flask was cooled in ice and 2:5-dichloro-1:3-dinitrobenzene (16 g.) was added. The mixture was stirred for 1½ hours in the cold and then refluxed for 6 hours with continued stirring. It was then extracted with 2% caustic soda solution (300 c. c.); the extract was cooled with ice and acidified with dilute nitric acid, when a red oil separated. This was allowed to settle, and left in a refrigerator overnight, when the greater part of the oil solidified. The supernatant aqueous layer was decanted off, the mixture was well shaken with 50 c. c. of alcohol and then filtered. The residue on the filter paper consisted of beautiful orange-red plates of 2:6-dinitro-4-chlorophenylacetoacetic ester. A further crop of the ester was obtained by allowing the filtrate to evaporate slowly, m.p 81° yield 12.5 g. (56% of theory). (Found: N, 8.51. C₁₂H₁₁O₇N₂Cl requires N, 8.47 per cent).

2:6-Dinitro-4-chlorophenylacetone.—2:6-Dinitro-4-chlorophenylacetoacetic ester (4 g.) was dissolved in concentrated sulphuric acid (50 c.c.), and water (25 c. c.) was then added to it without cooling, when a brisk evolution of CO_2 commenced. After this had ceased to evolve, the resulting black solution was poured on crushed ice, left in a refrigerator overnight and then filtered, when the crude ketone was obtained as a light brown powder. It was recrystallised by dissolving in hot alcohol, filtering and allowing the filtrate to evaporate by itself, when light brown needles of the ketone were obtained, m.p. $122-23^\circ$, yield theoretical. (Found: N, 10.99. $\text{C}_8\text{H}_5\text{O}_2\text{N}_2\text{Cl}$ requires N, 10.83 per cent).

The *phenylhydrazone* of the above ketone was obtained by refluxing the crude ketone (1 g.), dissolved in a small quantity of alcohol, with phenylhydrazine (1 c. c.) for 45 minutes. The solution was then cooled in ice, diluted with a small quantity of water and filtered. The dark coloured residue was dissolved in hot alcohol, filtered and the filtrate allowed to evaporate by itself, when the phenylhydrazone crystallised out as dark brownish red needles, m.p. $117-18^\circ$ yield 0.8 g. (59.4% of theory). (Found: N, 16.28. $\text{C}_{15}\text{H}_{13}\text{O}_4\text{N}_4\text{Cl}$ requires N, 16.06 per cent).

The *oxime* of the dinitrochlorophenylacetone was obtained by dissolving the ketone (1 g.) in hot alcohol, cooling, adding to it hydroxylamine hydrochloride (1.2 g.), followed by a drop of phenolphthalein and then caustic soda solution added drop by drop, till alkaline to phenolphthalein, and refluxing for three quarters of an hour. The greater part of the alcohol was then removed by distillation; the residue was cooled and then diluted with a small amount of water. The brown crystalline mass of the oxime that separated, was filtered off, dissolved in hot alcohol, filtered hot, and the filtrate allowed to evaporate by itself when very fine, light brown needles of the oxime were obtained, m.p. 111° , yield 1 g. (94.5% of theory). (Found: N, 15.36. $\text{C}_8\text{H}_5\text{O}_2\text{N}_3\text{Cl}$ requires N, 15.32 per cent).

2:6-Dinitro-4-chlorophenylacetic Acid.—2:6-Dinitro-4-chlorophenylacetoacetic ester (2 g.) was refluxed with 20% alcoholic potash (25 c.c.) and water (1.5 c. c.) for 1½ hours and the alcohol was then distilled off. The residue was acidified with dilute hydrochloric acid and the dark coloured crystalline mass that separated out, was filtered off. It was dissolved in alcohol, filtered, and the filtrate allowed to evaporate slowly. The dark brown crystals of the acid separating were further purified by dissolving in sodium carbonate solution, filtering and reprecipitating by hydrochloric acid, when the desired acid was obtained as a light brown powder. It does not melt, but decomposes on strong heating, yield 1 g. (63.4% of theory). (Found: N, 10.93. $\text{C}_8\text{H}_4\text{O}_6\text{N}_2\text{Cl}$ requires N, 10.75 per cent).

2-Methyl-3-carbethoxy-4-amino-6-chloroindole.—A mixture of 2:6-dinitro-4-chlorophenylacetoacetic ester (1.2 g.), iron powder (2.6 g.), crystallised ferrous sulphate (0.3 g.) and water (10 c. c.) was refluxed for 3 hours on a free but low flame. The mixture was then cooled with shaking in ice and filtered. The residue was extracted four times with 10 c. c. of alcohol each time, and the extract filtered hot. The filtrate which was first colorless, but turned dark violet in a very short time, was allowed to evaporate under cover, when the cyclised amine separated out as colorless crystals turning dark violet immediately on exposure to air. It begins to soften at 194° and

finally melts at 217° , yield 0.8 g. (87.3% of theory). (Found: N, 10.99. $C_{13}H_{13}O_2N_2Cl$ requires N, 11.09 per cent).

2:6-Dinitro-4-chlorophenylmalonic Ester.—The sodium derivative of malonic ester was obtained in the usual way from diethyl malonate (25 g.) and sodium (3.5 g.) in anhydrous ether (75 c. c.). When the last traces of sodium had disappeared, the flask was surrounded by ice and 2:5-dichloro-1:3-dinitrobenzene (12 g.) added. The mixture was stirred for one and a half hour in cold and then refluxed for 6 hours with continued stirring. It was then extracted with 2% caustic soda solution, the aqueous extract was cooled with ice, acidified with dilute nitric acid and left in a refrigerator overnight, when a red semi-solid mass settled down. The supernatant liquid was decanted off, the semi-solid mass dissolved in alcohol; the alcoholic solution filtered, and the filtrate allowed to evaporate slowly, when orange-red plates of the dinitrochlorophenylmalonic ester separated out, m.p. 85° , yield 4 g. (22% of theory). (Found: N, 7.88. $C_{13}H_{13}O_4N_2Cl$ requires N, 7.79 per cent).

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A NOTE ON THE EFFECT OF SURFACE ACTIVE AGENTS ON ACID ALKALI INDICATORS

BY RAM CHARAN MEHROTRA

In recent communications (Mehrotra, *Curr. Sci.*, 1947, **16**, 345; *Anal. Chim. Acta*, 1948, **2**, 36), the applicability of Congo red as adsorption indicator in argentometric titrations has been described. Congo red (diphenyl bisazo- α -naphthylamine-4-sulphonic acid) has been recommended for use as acid alkali indicator and it shows a change of colour from blue-violet to red in the p_H range of 3 to 5. In the above communications, it has been described that if the p_H be maintained at 3 to 5, then in the titration of Cl^- , Br^- , I^- , CNS^- ions against silver ions, a sharp colour change from blue (or green in the case of bromide and iodide) to red occurs on the coagulated particles in the more concentrated solutions. If the titrating solutions be dilute or if the silver halide be kept in the suspension phase by the addition of a protective colloid like dextrin, then the above colour change occurs in the suspension phase. Similarly, in the reverse titrations of silver ions against halide ions, the opposite colour change, red to blue (or green), occurs, even if the p_H of the solution is maintained at a constant value of 4. The observation is similar to those of a number of previous workers (Smith and Jones, *J. Phys. Chem.*, 1934, **38**, 248; Hartley, *Trans. Faraday Soc.*, 1934, **30**, 444; Hartley and Roe, *ibid.*, 1940, **36**, 106; Krishnappa, Doss and Rao, *Proc. Ind. Acad. Sci.*, 1946, **23A**, 47), who have shown that the surface active agents like the wetting agents Ipegon T (sodium salt of oleyl-N-methylamine) and Nekal BX affect the p_H of the medium in which they are shaken. In the present communication, similar observations are recorded for purely inorganic surface active agents.

A sodium acetate-acetic acid buffer solution was prepared having a p_H 4. To 10 c.c. of this buffer solution were added 10 c.c. of say $N/25$ -potassium chloride solution and about 1 c.c. of 2 % dextrin solution and a drop of 0.2% Congo red solution. Silver nitrate solution of nearly the same strength as the chloride solution was run in. The suspension remained blue in shade so long as the chloride ions were present in excess. Just with the addition of half a drop of the silver nitrate solution in excess, the suspension changed its colour suddenly from blue to red. The above colour change is quite reversible; if to the red suspension is added a drop or two of the chloride solution, it again becomes blue. If we consider the change in the p_H of the solution, then the addition of a drop of silver nitrate or the chloride solution cannot be expected to produce any change in the p_H of the suspension. If the silver nitrate solution affects the p_H of the suspension at all, it can have the tendency to make the suspension, if unbuffered, a little more acidic owing to its hydrolysis, and hence any colour change due to p_H alone should turn the indicator more blue, rather than red. To obviate any possible source of the change in the acidity of the suspension, the observations were taken in a buffered solution. Hence, the above colour changes cannot be explained on the change of the acidity of the suspension.

The observations can, however, be easily explained if we take into account the part played by the surface of the silver halide molecules. The surface of the silver chloride is charged positively in the presence of excess of silver ions due to the adsorption of the silver ions (Lottermoser, *J. prakt. Chem.*, 1905, ii, 72, 39; 1906, 73, 374), and this positively charged surface exerts a powerful attraction towards the red anions of the indicator, which are preferentially adsorbed. Hence, the equilibrium



is shifted towards the right and the suspension exhibits a colour change towards red. In the reverse case, the particles of silver halide being negatively charged in the presence of excess halide ions adsorb the blue cations of the indicator preferentially and the equilibrium shifts towards the left with the suspension changing blue in shade. Thus, though the p_H of the medium remains constant, the colour change of the acid alkali indicator is brought about by the change in the sign of the charge on the surface of the silver halide particles.

A similar observation has been made by Berg and Becker (*Z. anal. Chem.*, 1940, 119, 81) with their newly discovered indicator Indoxine (5:8-quinoline-quinone-8-hydroxy-5-quinolyl-5 imide) which they have recommended both as acid alkali as well as adsorption indicator. In acid alkali titration, the dye changes its colour from red to blue in the p_H range of 6 to 8. They have shown that if a chloride solution is taken, maintained acidic by acetate buffer and a drop or two of the indicator added, then the addition of silver nitrate solution in excess turns the colour of the precipitate from red to blue and *vice versa*. The cause of the effect is similar to that described above.

Similar effects have been observed with $(\text{BaSO}_4)\text{Ba}^{++}$ micelles which have been shown to adsorb Congo red with the development of red colour (Riegel and Ridson, *Kolloid Z.*, 1933, 64, 304).

Thus, as the above observations show, the colorimetric determination of p_H of solutions is affected by not only the organic surface active agents like Ipegon-T and Nkal BX, but also by the inorganic surface active materials like the positively or negatively charged precipitates and suspensions and hence care should be taken that they should not be present while determining the p_H of a solution colorimetrically.

Further quantitative work on the apparent shift of p_H in the above cases is in progress.

In conclusion, the author wishes to thank Prof. N. R. Dhar for his interest and encouragement.

APPLICATION OF HAMMICK AND ANDREW'S MIXTURE LAW FOR SOLUTES IN WATER

BY W. V. BHAGWAT, S. N. KAWERSHWAR AND R. C. SAXENA

It is shown that though mixture law is applicable to parachor of liquid-liquid mixtures, very low results are obtained when a solid solute is used. This has been supported by Hammick and Andrew's work and by the work of S. K. Ray, although they themselves have failed to observe this. In case of liquid mixtures, when water is one of the constituents, acetic acid shows normal behaviour and p_r can still be calculated in case of ethyl alcohol, methyl alcohol and acetone by extrapolation ($x=1$).

Hammick and Andrew (*J. Chem. Soc.*, 1929, 754) showed that mixture law may be applied to determine the value of parachor of a solute in a solvent. They selected liquid mixtures and established that for non-associated solutes in non-associated solvents the values obtained for the parachor from the measurements on solutions are in excellent agreement with those found for the pure liquids. Associated solutes also showed an excellent agreement both in non-associated and associated solvents. They have concluded that the mixture method can be used by extrapolation to determine the parachors of liquid solutes even if the simple mixture law does not apply.

However, the work of Hammick and Andrew (*loc. cit.*) is limited to liquid mixtures only and in all cases organic solvents have been used. Hammick and Andrew (*J. Chem. Soc.*, 1934, 33) have applied the mixture law in one case to a mixture containing a solid and a liquid and have observed that the results in solution are lower by 30 units. Following are their results.

TABLE I

Tetranitromethane in benzene at 25.6°.

x .	d_{4}^{25} .	r_s	M_m .	P_m .	P_x .
0.0	0.8737	28.23	78.05	206.0	—
0.3377	1.169	27.49	117.95	231.1	280.4
0.5082	1.302	27.70	138.0	243.2	279.1
0.6736	1.419	28.19	157.5	255.8	280.0
0.8561	1.540	28.92	179.0	269.6	280.3

$P_{(calc.)} = 301.2$ Mean $P_r = 280.0$

The work has been extended by Ray (*J. Indian Chem. Soc.*, 1934, 11, 671 ; 1935, 12, 248) and he finds that the mixture law (simple and straight line) is applicable in case of solutions of solids in liquids. Ray's results (*loc. cit.*) are summarised in Table II.

TABLE II

Solvents.	Solutes.	Variation of x .	Variation of P_x .
Benzene	Naphthalene	0.331-0.095	312.6-310.7
CCl ₄	"	0.037-0.109	312.3-310.2
Chloroform	"	0.034-0.071	338.1-334.7
Pyridine	"	0.029-0.049	335.4-334.6
Benzene	8-Oxyquinoline	0.018-0.046	320.3-322.8
Nitrobenzene	Anthracene	0.010-0.011	419.1-416.5

In spite of these results Ray concludes that the parachor obeys straight line mixture law in dilute solutions. It will be observed that ' x ' varies from $M/100$ to $M/10$ in extreme cases. The sudgen's method of calculating parachor admits an error to the extent of 0.5% to 1%. This percentage of error is therefore possible in P_m . Hence, when P_x is calculated by the mixture law,

$$P_m = xP_x + (1-x)P_s$$

and the concentration varies from $M/100$ to $M/10$, the error may get magnified 100 to 10 times. Thus, the variation observed by Ray at such dilutions cannot be due to the applicability of the straight line mixture law. Moreover, in many cases the variation is not proportional to the concentration of the solute, and in some cases the parachor value falls instead of increasing as the concentration of the solute is increased. A comparison of his mean observed results and the calculated results is interesting and is shown in Table III.

TABLE III

Solvent.	Solute.	P_{mean} .	$P_{\text{calc.}}$	Solvent.	Solute.	P_{mean} .	$P_{\text{calc.}}$
Benzene	Naphthalene	311.8	313	Benzene	8-Quinoline	322.0	323.6
CCl ₄	"	311.6	"	CCl ₄	"	315.0	"
Chloroform	"	335.4	"	Chloroform	Xanthene	420.8	420.0
Pyridine	Naphthol	334.5	333	Pyridine	"	421.8	"
Ethylacetate	"	322.0	"	Benzene	Phenanthrene	417.2	418.0
Benzene	Coumarin	311.0	314	CCl ₄	"	467.1	"
Chloroform	"	313.7	"	Acetone	"	361.0	"
Pyridine	"	318.0	"	Nitrobenzene	Anthracene	417.8	418.0

These results clearly show that in organic solvents the solute obeys the simple mixture law, although the results in pyridine are at variance due to the fact that pyridine does not behave as 'normal solvent'. We do not understand how Ray has come to the conclusion that the straight line mixture law is applicable. The variation between the mean results and the calculated results is about 0.5%, and hence the difference is within

the experimental error. In a series of papers published from our laboratories (*J. Indian Chem. Soc.*, 1942, **19**, 225, 149, 153, 492; 1944, **21**, 54, 61, 180, 386; 1945, **22**, 52, 111, 114, 116, 312) we have shown that when a solid is dissolved in a solvent the observed values in general are smaller than the calculated values, and that there is no relation between concentration and P_{obs} . *e. g.* the straight line mixture law does not hold. Thus, the observations of Hammick and Andrew in case of liquid-liquid mixtures are not borne out in case of solid-liquid mixtures. In cases where the solvent is water, this deviation is more marked. Further, if the solid is an electrolyte and the solvent is water, the deviation from the mixture law is the greatest. Hammick and Andrew (*loc. cit.*) state that in water anomalous results are obtained, but they have done no work. Following table shows our results.

TABLE IV

Temp. = 25°.

Acetic acid in ethyl acetate.					Methyl alcohol in water.				
Conc.	$d.$	$r.$	$P_m.$	$P_x.$	Conc.	$d.$	$r.$	$P_m.$	$P_x.$
0.6613	0.9757	25.35	159.8	131.3	0.1980	0.9479	43.20	56.18	75.75
0.7577	0.9943	25.58	151.5	131.2	0.3761	0.9120	36.35	62.60	79.40
0.8204	1.007	25.70	145.5	131.2	0.5306	0.8784	31.01	68.28	82.40
0.8672	1.015	26.30	142.9	131.8.	0.7305	0.8403	27.40	76.85	85.96
					1.0000	0.7931	23.65	—	88.95
Ethyl alcohol in water.					Acetic acid in water.				
0.1995	0.9305	31.07	59.87	90.22	0.2176	1.049	40.06	65.12	111.8
0.2370	0.9219	30.92	64.45	102.80	0.3427	1.059	36.96	75.39	119.8
0.5542	0.8504	26.33	89.30	119.10	0.6591	1.063	30.98	101.8	126.8
0.6697	0.8324	25.54	99.28	122.50	0.8154	1.058	29.38	114.9	129.0
0.8377	0.8098	24.35	113.70	125.60	1.0000	1.051	27.10	—	130.4
1.0000	0.7894	22.59	—	127.10					

According to Hammick and Andrew (*loc. cit.*), associated solutes give parachor values by the solution method both in non-associated solvents and associated solvents which are in excellent agreement with those observed for the pure liquid at the same temperature. Our results with acetic acid in ethyl acetate support these observations. In case of methyl and ethyl alcohols and acetic acid in water, the simple mixture law is not applicable, but the variation in the value of P_x with concentration indicates that the parachor of the solute can still be calculated by extrapolation ($x=1$). The results in water therefore are not anomalous as predicated by Hammick and Andrew (*loc. cit.*).

CHEMISTRY DEPARTMENT,
HOLKAR COLLEGE,
INDORE.

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THE REACTION BETWEEN MERCURY AND NITRIC ACID. A KINETIC STUDY

By A. N. KAPPANNA AND K. M. JOSHI

When mercury is added to nitric acid, kept continuously stirred, in the range of concentrations of $4N$ to $7N$, the dissolution of the metal starts after an interval of time which may be designated the period of passivity. This period of passivity is greater in more dilute solutions than in more concentrated ones for a given rate of stirring.

The period of passivity in nitric acid solutions of a given concentration depends upon the rate of stirring, being greater in more rapidly stirred solutions.

The period of passivity is marked by the accumulation of nitrous acid in solution, until the concentration of nitrous acid at 22° reaches near about $0.0012N$ whereafter dissolution of mercury commences.

The period of passivity disappears if the nitric acid contains initially added nitrous acid in sufficient quantities.

After the period of passivity, the rate of dissolution is greater in more concentrated solutions than in less concentrated ones at a constant rate of stirring. In nitric acid solutions of the same concentration, the rate of dissolution slows down with increase in the rate of stirring.

A mechanism has been suggested for the dissolution of mercury in nitric acid. Nitrous acid is assumed to be the dissolving agent. The initial formation of nitrous acid is assumed to be due to the catalytic decomposition of nitric acid on the surface of mercury, the mercury surface forming an oxygen adsorption complex. The period of passivity has been explained as due to the retarding influence of nitric acid on the dissolving effect of nitrous acid and the period ending with the attainment of a critical concentration of nitrous acid in the reaction mixture.

Mercury belongs to that class of metals which do not ordinarily liberate hydrogen from nitric acid. The products formed in the reaction vary considerably with the conditions under which the reaction is allowed to take place. Literature on the subject is quite vast. From a kinetic viewpoint, however, the only extensive investigation on record is that of Veley (*Phil. Trans.*, 1891, **A**, 182, 279). Although it was known before, Veley showed conclusively that stirring of nitric acid in contact with mercury retarded the reaction. Veley further established that this retardation was due to the removal by stirring of the nitrous acid formed at the interface away from contact with the metal and that it was the initially formed nitrous acid that catalysed the dissolution of the metal. Hedges (*J. Chem. Soc.*, 1930, 561) studied the rate of dissolution of copper in nitric acid, and found the rate of dissolution to vary inversely with the rate of stirring and the attack of the metal by the acid could be prevented for quite a considerable length of time by increasing the stirring rate to 2000 r.p.m. Doubtless, similar data could be obtained with mercury in agitated nitric acid. It was the object of the present investigation to collect more information on the nature of the reaction between mercury and nitric acid. The points investigated relate to (1) whether and in what manner the period of passivity is dependent on the concentration of nitric acid and the rate of stirring, and (2) in what way does the rate of dissolution, when once dissolution commences, vary with the concentration of the acid and the rate of stirring.

E X P E R I M E N T A L

The nitric acid used was of the guaranteed reagent quality. The stock acid showed the presence of nitrous acid. The removal of nitrous acid was effected by warming the acid to a temperature not exceeding 40° and agitating the acid by passing a stream of purified air. The passage of air was continued until tests (with an acetic acid solution of sulphanilic acid and α -naphthylamine) proved the complete absence of nitrous acid. The acid was then cooled and diluted to the desired extent.

Chemically pure double-distilled mercury was further purified by first shaking the metal with a dilute solution of potassium cyanide and sodium peroxide and washing it with distilled water. It was next repeatedly allowed to flow in thin stream through a long column of dilute nitric acid in which a small quantity of mercurous nitrate had been dissolved, and thereafter washing it by thorough shaking with air-free distilled water a number of times. It was then stored in glass-stoppered bottles under air-free distilled water. Immediately before use, this mercury was again washed with air-free distilled water.

The reaction was studied in large-sized Jena glass beakers (10 cm. diameter and 1.5 litre capacity). All-glass stirrers, rotated by an electric motor with arrangements for regulating speed, were employed. These were fixed in a framework and the positions of beakers in all experiments were adjusted in such a way that the stirrers were always situated at the centres of the beakers and the bottom blades of the stirrers were at a constant height above the surface of mercury.

One litre of nitric acid solution of the desired concentration was taken in the beaker and stirring started. When the rate of stirring was adjusted and became steady, mercury (50 c.c.) was taken in a burette and run into the nitric acid solution, care being taken to see that the tip of the burette was well underneath the surface of the nitric acid solution to ensure that mercury did not stream through air before getting into the nitric acid. This precaution was found necessary, as we observed that mercury, allowed to come in contact with air freely before entering nitric acid solution, did not always give reproducible results. The reason for this probably is the varying nature of the laboratory atmosphere. By observing the aforementioned precaution, however, we were able always to obtain reproducible data.

Immediately after the addition of mercury, as well as at intervals later, 10 c.c. samples of nitric acid solution were pipetted out and tested for nitrous acid and mercury.

All the experiments detailed below were carried out at 22° .

Preliminary experiments, carried out with nitric acid solutions in the range of concentrations of $4N$ to $7N$, show that, when mercury is added to nitric acid which is already being stirred :—

(i) There is an interval of time which may be termed "the period of passivity" when the metal does not go into solution in nitric acid. This period has a constant magnitude for a given concentration of the acid and a particular rate of stirring but it varies both with concentration and rate of stirring.

(ii) During the period of passivity, when no trace of mercury could be detected in the solution, nitrous acid is continuously formed.

(iii) At a particular stage, which is the end of the period of passivity, dissolution of mercury commences and when once it commences, goes into solution rapidly and with continuously increasing tempo.

(iv) Under the conditions of our experiments the entire quantity of mercury going into solution is present as mercurous mercury.

Period of Passivity

A set of experiments was carried out to determine the influence of the concentration of the acid and the rate of stirring on the period of inactivity. The end of this period was reckoned by noting the time after the start of the experiment, when the first trace of mercury was detected by spot reaction with *p*-dimethylaminobenzilidene-rhodamine.

Table I gives the results of these experiments.

TABLE I

Conc. of acid (N)	...	6	6	6	7	5	5	5	4
Rate of stirring (r. p. m.)	400	650	1000	1000	250	400	650	250	
Period of passivity (min.)	8	15	70	10	45	90	150	300	

The period of passivity appears from the table to depend both on the rate of stirring and on the concentration of the acid.

Formation of Nitrous acid during the Period of Passivity

As mentioned above, nitrous acid is continuously formed during the period of passivity. Ten c.c. of the reacting nitric acid were withdrawn from the beaker at intervals, diluted with 40-50 c.c. of water and titrated against *N*/200-permanganate solution and the concentration of nitrous acid calculated from the titre. Table II gives the results of two experiments.

TABLE II

Conc. of $\text{HNO}_3 = 4.61N$. Rate of stirring = 450 r. p. m.		Conc. of $\text{HNO}_3 = 5.0N$. Rate of stirring = 600 r.p.m.	
Time after addition of mercury.	Conc. of nitrous acid in equiv. per litre.	Time after addition of mercury.	Conc. of nitrous acid in equiv. per litre.
0 min.	0	0 min.	0
88	0.00044	50	0.00024
120	0.00104	110	0.00080
135	0.00108	125	0.00124
153	0.00120		
After this, mercury was found in solution.		After this, mercury was found in solution.	

Experiments carried out with other concentrations of nitric acid and other rates of stirring show that under varied conditions, the dissolution of the metal commences invariably when the concentration of nitrous acid reaches a value between 0.0012*N* and 0.00125*N*.

Rate of Dissolution of Mercury after the Period of Passivity.—It has been stated earlier that when dissolution takes place under conditions when nitric acid is kept continuously stirred, the entire quantity of mercury going into solution does so in the mercurous state. Ten c. c. samples of the reaction solution were pipetted out at intervals after the period of passivity, diluted and the mercury was precipitated as mercurous chloride with all the necessary precautions. The precipitate was collected in Gooch crucibles, washed, dried below 90° and weighed. The amount of mercury per litre of solution was calculated from the weight of mercurous chloride. Tables III to VI contain the results of a few experiments.

TABLE III

Conc. of acid = 5*N*.
Rate of stirring = 500 r.p.m.
Period of passivity = 90 minutes.

Time after period of passivity.	Wt. of Hg /litre of solution.
3 min.	0.1197 g.
18	0.1535
48	0.4418
78	1.1088
108	3.5176

TABLE IV

Conc. of acid = 6*N*.
Rate of stirring = 400 r.p.m.
Period of passivity = 8 minutes

Time after period of passivity.	Wt of Hg /litre of solution.
1 min	0.4418 g.
15	6.0631
28	8.4307
48	64.4900
63	126.0800

TABLE V

Conc. of acid = 6*N*. Rate of stirring = 650 r.p.m. Period of passivity = 15 minutes.

Time after period of passivity.	Wt. of Hg/litre of solution.
12 min.	2.9059 g.
25	8.0575
42	24.6921
53	43.1548
68	71.3378

TABLE VI

Conc. of acid = 6*N*. Rate of stirring = 1000 r.p.m. Period of passivity = 70 minutes

Time after period of passivity	Wt. of Hg/litre of solution
15 min	0.2209 g.
50	0.9177
80	4.3758
110	7.8000

In all these cases it can be seen that the rate of dissolution indicates the existence of autocatalytic action.

We have found by simultaneous estimation of nitrous acid that the amount of nitrous acid was at all times far in excess of the quantity of mercury in solution. These results have not been included here, because under the best conditions, we could not attach quantitative importance to these analyses on account of the fact that once dissolution starts, nitrous fumes are evolved in copious quantities and even where colorimetric methods were employed, we could not convince ourselves of the accuracy of our determinations.

Nevertheless, there appears little doubt that the quantity of nitrous acid is always, after the period of passivity, in large excess over the quantity corresponding to the formation of mercurous nitrite. We are mentioning this here as a plausible reason for the autocatalytic nature of the dissolution.

It will be observed from Tables III to VI that for a given concentration of acid, even as the period of passivity becomes greater with increase in the rate of stirring, the rate of dissolution falls very considerably with increase in the rate of stirring.

Influence of Initially added Mercurous Nitrate.—A few experiments were carried out to see if mercurous ion, initially present, would influence either the period of passivity or the rate of dissolution thereafter in any way. The results in all cases show that mercurous ion has no influence. We have not therefore included these results here.

Influence of Initially present Nitrous Acid on the Period of Passivity and Rate of Dissolution.—A standard solution of sodium nitrite, prepared from a purified sample of the salt, was added in different quantities to solutions of nitric acid (being stirred) before the addition of mercury and the effect studied. It is assumed that the concentration of the initially present nitrous acid is equal to the concentration of sodium nitrite. Tables VII to X contain a few of the results.

TABLE VII

Conc. of acid = 4*N*.
Rate of stirring = 450 r.p.m.
Initial conc. of HNO_2 = 0.00780*N*.
Period of passivity = Nil.

Time.	Wt. of Hg/litre of soln.
30 min.	0.06799 g.
45	0.0850
75	0.2549
140	0.5863
190	0.9346

TABLE VIII

Conc. of acid = 4*N*.
Rate of stirring = 450 r.p.m.
Initial conc. of HNO_2 = 0.0156*N*.
Period of passivity = Nil.

Time.	Wt. of Hg/litre of soln.
30 min.	0.2379 g.
45	0.4263
75	0.5778
140	0.9686
190	1.3765

TABLE IX

Conc. of acid = 5N.
 Rate of stirring = 650 r.p.m.
 Initial conc. of HNO_2 = 0.0039 N.
 Period of passivity = Nil.

Time.	Wt. of Hg /litre of soln.
15 min	0.0339 g.
38	0.3229
54	0.7817
83	2.7800

TABLE X

Conc. of acid = 5N.
 Rate of stirring = 650 r.p.m.
 Initial conc. of HNO_2 = 0.0078N.
 Period of passivity = Nil.

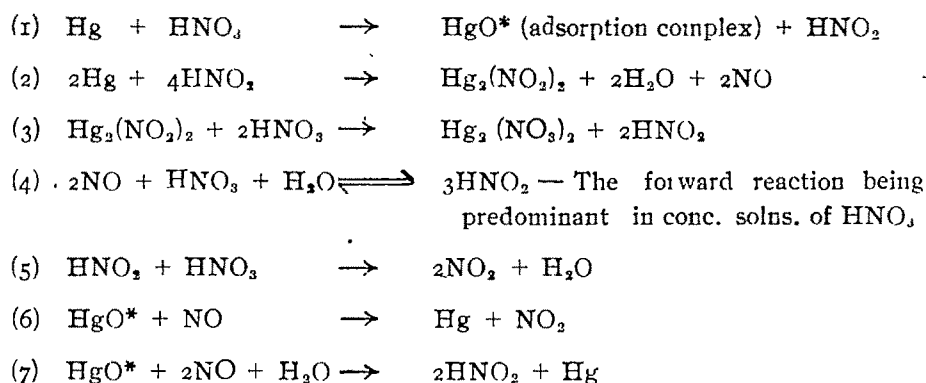
Time.	Wt. of Hg /litre of soln.
5 min.	0.1605 g.
18	0.5693
38	1.5044
54	2.5575
83	4.7014

These results indicate clearly that the rate of dissolution definitely increases with increase in the initial concentration of nitrous acid. It will be noted that the initial concentration of nitrous acid in each of the cases above is much higher than the critical concentration of nitrous acid (spontaneously formed in contact with mercury) necessary to start dissolution. It is not surprising therefore that there is no period of passivity. We have carried out experiments with initial concentrations of nitrous acid slightly below and slightly above 0.0012N. In cases where the initial concentration of nitrous acid was below 0.0012N, a period of passivity was observed until the concentration of nitrous acid in solution reached round about this value before dissolution started. We chose 4N solutions of nitric acid for these experiments as the period of passivity in this solution even at the low rate of stirring of 250 r. p. m. was as high as 5 hours, and any differences that altered conditions might create would be more pronounced. Tables VII and VIII show unmistakably the effect of initial addition of nitrous acid.

DISCUSSION

In arriving at or suggesting any particular mechanism for the reaction between nitric acid and mercury or any other metal, it is necessary to confine ourselves to the particular condition of the experiments in which the nitric acid is kept continuously stirred before the metal is brought in contact with acid. In the case of copper, Hedges (*loc. cit.*) has observed the formation of a visible oxide film on the surface and therefore the dissolution of the metal in nitric acid or nitrous acid, as may be the case, is suggested to be through the formation of this oxide. This may be a correct mechanism for copper. We have tried to make careful observations in our experiments during the period of passivity, and we have not been able to observe any change in the appearance of mercury surface in contact with agitated nitric acid during this period. In any case, we have no grounds to infer that a visible oxide film, which is in any way distinguishable from the mercury surface itself, is formed before dissolution starts. The initial formation of nitrous acid from nitric acid and its accumulation up to a definite concentration before dissolution of mercury starts, remains a fact that should

be explained, in our opinion, on a slightly different basis. To suggest that nitrous acid is formed by the catalytic decomposition of nitric acid on mercury surface without either any visible evolution of oxygen or the formation of an oxide, would call for a mechanism something akin to the formation of an adsorbed oxygen layer on the surface of mercury. The question would then be how does the oxygen layer help in starting dissolution? Does it help at all, and if so, in what way? It is pertinent here to recall the results of Veley (*loc. cit.*) where he proves that nitrous acid dissolves mercury quite readily and the influence of nitric acid on this reaction is to retard the dissolution. One has to conclude therefore that in the reaction between mercury and nitric acid, nitric acid as such does not react with and dissolve mercury at all, particularly under the conditions of the experiments carried out in the present investigation, but the cause of the dissolution of mercury is the nitrous acid formed initially, as we have suggested here, by catalytic decomposition at the surface of mercury. This view is further substantiated by our observation that nitrous acid formation oversteps in rate the dissolution of mercury, after the period of passivity. We would therefore suggest the following mechanism:—



The reactions involving the formation of nitrous acid are assumed to predominate in rates over the reactions involving the disappearance of the acid.

Period of Passivity.—It now remains to explain the cause for the period of passivity and its variation with the rate of stirring. Nitrous acid happens to be the dissolving agent. Why then does it accumulate up to a concentration of about 0.0012*N* in the nitric acid solution before it acts upon mercury? Here again we have to draw support from the experiments of Veley relating to the retarding influence of nitric acid on the dissolving effect of nitrous acid.

While nitrous acid is capable of dissolving mercury, it would not be correct to assume that the heterogeneous reaction is either rapid or as one not involving large energy of activation. At very low concentrations of nitrous acid, as in the initial stages of its formation, the rate of reaction is unnoticeable. Added to this we have to take note of the fact that nitric acid present in large quantities has great retarding effect on this reaction and this retarding effect would be rather highly pronounced when only traces of nitrous acid happen to be present. Under these opposing forces tending

towards retarding the dissolution, however, a stage must be reached when the retarding effect should be just overcome by the increasing concentration of nitrous acid ; and this stage appears to be reached near about the concentration of 0.0012*N* at the temperature at which we have carried out the experiments.

Our observations, as stated earlier, lead to the conclusion that the rate of formation of nitrous acid at the surface of mercury is itself an autocatalytic reaction, and the rapidity with which the nitrous acid formed at the surface could be removed therefrom would determine the rate of accumulation of nitrous acid in the bulk of solution *i. e.* if the rate of stirring is increased, the rate of formation of nitrous acid at the surface is naturally diminished. Hence, the delay in the nitrous acid concentration attaining the required critical value when rate of stirring is increased. The increase in the period of passivity with increase in the rate of stirring thus becomes understandable.

The mechanism and the explanation suggested above pertain mostly to the reactions leading to the commencement of dissolution. Once dissolution commences, the formation of oxides of nitrogen further complicates the processes. The surface reactions including dissolution of mercury still appear to be determined and dominated by the period of contact of the products with the surface and with increased rates of stirring, we observe, for the same concentration of acid, the rate of dissolution falls as shown in the following table.

TABLE XI

Conc. of acid.	Revolutions per minute.	Passivity period.	Amount of Hg dissolved in about the same time after passivity.
6 <i>N</i>	400	8 mins.	64.49 g. (48 mins.)
6	650	15	43.1548 g. (53 ,,)
6	1000	70	0.9177 g. (50 ,,)

DEPARTMENT OF CHEMISTRY,
COLLEGE OF SCIENCE, NAGPUR.

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PRODUCTION OF THE JOSHI EFFECT IN OXYGEN UNDER SILENT
ELECTRIC DISCHARGE. PART III. COMPARATIVE STUDIES
UNDER THE VISIBLE AND THE QUARTZ ULTRAVIOLET

BY S. R. MOHANTY

The Joshi effect Δi has been observed in pure oxygen (250 mm.) enclosed in a Siemens' tube with a quartz window for end on irradiation, and excited by 2 to 5 kV of 50 cycles frequency. Δi is greater in Hg light (29.2%) than under a (glass) incandescent bulb (16.9%), and is reduced to the latter when the ultraviolet is cut off.

That the magnitude of the Joshi effect Δi in chlorine increases from the infra-red to the ultraviolet, i.e., frequency-wise, has been observed by Joshi (*Proc. Indian Sci. Cong.*, 1943, Part II, pp. 70-75; *Curr. Sci.*, 1945, **14**, 317). The author and Kaniath (Part II, this *Journal*, 1948, **25**, 467) have shown that Δi in oxygen under the visible is greater in the blue than in the green-red. The results of a preliminary investigation of the author (*Proc. Indian Sci. Cong.*, 1948, Part III, *Chem. Sec.*, Abst. No 35) having revealed that Δi in oxygen is greater under the total radiations from a quartz mercury vapour lamp than under the visible, it was of interest to study in some detail the production of the effect Δi in oxygen under the ultraviolet.

E X P E R I M E N T A L

The discharge vessel consisted of a Siemens' all-glass ozoniser which had a quartz window cemented on one end. It was filled with purified oxygen at 250 mm. (25°) pressure, and excited by potentials V of 50 cycles frequency varied over 2 to 5 kV (r. m. s.). A Cambridge vacuo-junction was used as the A. C. indicator. The inner

TABLE I

*Comparative studies of the Joshi effect in oxygen under the visible and
the quartz ultraviolet.*

$pO_2 = 250$ mm. (25°). Temperature = 25°. Frequency of A. C. supply = 50 cyc./sec. Detector = Vacuo-junction. Sources of irradiation = Quartz mercury vapour lamp and 200 volt, 200 watt (glass) bulb, 15 cm. from the ozoniser

Irradiation parallel to the axis of the ozoniser

Quartz mercury vapour lamp										
V in kilo- volts (r. m. s.)	Quartz window				Quartz window & glass plate			200 Volt, 200 watt (glass) bulb		
	i_p	i_L	Δi	% Δi	i_L	Δi	% Δi	i_L	Δi	% Δi
2.67	5.1	3.61	1.49	29.2	4.12	0.98	19.2	4.24	0.86	16.9
2.93	7.14	5.48	1.66	23.3	6.16	0.98	13.7	6.25	0.89	12.5
3.2	9.59	7.94	1.65	17.2	8.60	0.99	10.3	8.72	0.87	8.9
3.47	11.40	9.7	1.70	14.9	10.3	1.1	9.6	10.40	1.00	8.8
3.73	12.49	10.73	1.76	14.1	11.23	1.26	10.1	11.40	1.09	8.7
4	13.19	11.32	1.87	14.2	12.17	1.02	7.7	12.37	0.82	6.2
4.27	13.96	12.13	1.83	13.1	13.04	0.92	6.6	13.23	0.73	5.2

tube of the ozoniser was filled with a concentrated solution of potassium permanganate which served to absorb all light; the ozoniser was also wrapped in black paper, except at the quartz window, to screen against external light. Current observations were made at different V in dark; when irradiated through the quartz window, in the end-on position, with a quartz mercury vapour lamp, when the ultraviolet portion of the above radiations was cut off appreciably by the superposition of a 2 mm. glass plate over the quartz, and with a 200 volt, 200 watt incandescent (glass) bulb placed in the position of the mercury lamp. In Table I is recorded but one typical set of observations.

DISCUSSION

The foregoing results show that despite restricted irradiation, Δi in oxygen under the ultraviolet is appreciable, being as high as 29.2% current-decrease at 2.67 kV; this is indicative of the large magnitude of the Joshi effect that can be produced under favourable conditions. The values of both Δi and $\% \Delta i$ for the quartz mercury vapour lamp and only the quartz window are higher than those obtained with the 200 volt, 200 watt incandescent (glass) bulb. Thus *e. g.*, at the above V , whilst Δi and $\% \Delta i$ are respectively 1.49 and 29.2 with total radiations from the mercury lamp, the corresponding values with the bulb are 0.86 and 16.9. Further, the effect due to the mercury lamp is reduced markedly on the addition of a 2 mm. thick glass plate over the quartz window, the values for Δi and $\% \Delta i$ thus obtained being sensibly similar to those observed under visible light. Thus, at the above V , $\% \Delta i$ is 29.2 without, and 19.2 with the glass plate; that with the incandescent (glass) bulb is 16.9. It is known that variation in Δi due to intensity fluctuations is not appreciable at high light-intensities, as long as the effective mean frequency is not altered (Joshi, *loc. cit.* Mohanty and Kamath, *loc. cit.*). It follows therefore that the relatively high magnitude of the effect under irradiation with the mercury lamp and only through the quartz window may be attributed to the high frequencies in the radiations, and not so much to their greater over-all intensity compared with those from the bulb.

Oxygen has a number of absorption bands in the ultraviolet (Liveing and Dewar, *Phil. Mag.*, 1888, **26**, 286; Lyman, *Astrophys. J.*, 1908, **27**, 87; Wartenberg, *Physikal. Z.*, 1910, **11**, 1168; L. and E. Bloch, *Compt. rend.*, 1914, **168**, 1161; Duclaux and Jeantet, *ibid.*, 1921, **173**, 581; Shaver, *Trans. Roy. Soc. Canada*, 1921, **15**, 7; Füchtbauer and Holm, *Physikal. Z.*, 1925, **26**, 345; Schmidt, *Z. Physik*, 1925, **31**, 475; Leifson, *Astrophys. J.*, 1926, **63**, 73; Dufay, *Compt. rend.*, 1929, **188**, 162; Granath, *Phys. Rev.*, 1929, **34**, 1045). In view of the fact, however, that despite absorption in the green and the red, Δi in oxygen for these wave-bands is but small (Mohanty and Kamath, *loc. cit.*), it is unlikely, as has been postulated by Joshi (*loc. cit.*), that the effect Δi is a consequence of selective light absorption.

The author's grateful thanks are due to Professor S. S. Joshi for having suggested the problem, and for his instructive advice and kind encouragement during the work.

PRODUCTION OF THE JOSHI EFFECT IN OXYGEN UNDER SILENT ELECTRIC DISCHARGE. PART IV. INFLUENCE OF TEMPERATURE

By S. R. MOHANTY

Influence of temperature t on the Joshi effect Δi in oxygen, enclosed in a (sealed) Siemens' type glass ozoniser at 331 mm. pressure (32°), has been studied over 30° to 125° and 2 to 5 kilo-volts of 50 cycles frequency. At a constant applied V, the discharge current i increases markedly with t . The increase with t of the mobility of ions has been shown to be small. The current rise is attributed therefore to the increase with t of the dielectric conductivity, and from Joshi's equation of the dielectric constant, of glass. The net effect Δi at constant V increases with t up to 50° and then decreases. The relative effect $\% \Delta i$, on the other hand, decreases progressively. According to Joshi, formation on the excited electrodes of a boundary layer derived, in part, from a wall-adsorption of ions and other particles in the discharge space is primary to Δi . Electrons released from this layer on irradiation are captured by the electro-negative gas-elements to form negative ions which produce Δi . Temperature would cause desorption and depolarization of the particles constituting the boundary layer, and would inhibit negative ion formation. Decrease of Δi , as observed, follows.

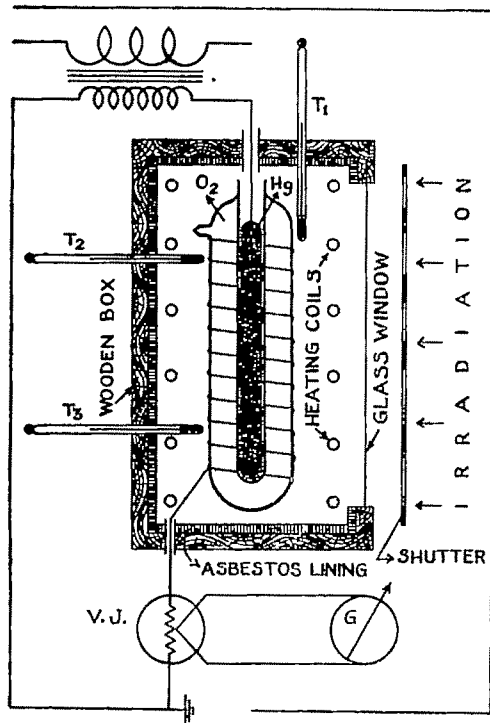
The marked dependence of the magnitude of the Joshi effect Δi on temperature t has been pointed out by Joshi (*Proc. Indian Sci. Cong.*, 1943, Part II, pp. 70-75). Joshi and Kuppaswamy (*ibid.*, 1941, Part III, *Chem. Sec.*, Abst. No. 35) found that Δi in chlorine decreases with t . Essentially similar were the observations of Deo and co-workers (Deo and Padmanabhulu, *ibid.*, 1944, Part III, *Chem. Sec.*, Abst. No. 36, Deo and Urs, *ibid.*, 1945, Part III, *Phys. Sec.*, Abst. No. 16) in chlorine, of Subba Rao and Shanmukha Rao (*ibid.*, 1944, Part III, *Chem. Sec.*, Abst. No. 37) in hydrochloric acid gas, and of Lahiry (*ibid.*, 1945, Part III, *Chem. Sec.*, Abst. No. 27) in iodine vapour in equilibrium with the solid. In view of the absence, apart from the preliminary observations of the author (*ibid.*, 1948, Part III, *Phys. Sec.*, Abst. No. 13), of data in the literature of this Δi phenomenon on the influence of temperature on the Joshi effect in oxygen, it was of interest to extend the above work to this gas, activated by the silent discharge.

EXPERIMENTAL

The experimental arrangement and the electrical circuit are shown in Fig. 1. A sealed Siemens' type glass ozoniser containing purified oxygen at 331 mm. pressure (32°) constituted the discharge vessel. It was enclosed in an asbestos-lined wooden box which had a glass window on one side. The interior of the box was heated electrically, temperature being regulated by varying the current through the heating coils. Temperature was recorded at three different positions with thermometers T_1 , T_2 and T_3 , and was kept constant at a desired value for at least 30 minutes before commencing a series of Δi observations.

The high tension terminal of the ozoniser was represented by mercury contained in the

FIG. 1



inner tube. A helix of copper wire (the distance between consecutive turns being sufficiently large to permit irradiation of the enclosed gas) on the outer tube constituted the low tension terminal. The oxygen tube was excited at different V in the range of 2 to 5 kV of 50 cycles frequency. The discharge current i was observed with a sensitive mirror galvanometer actuated by a Cambridge vacuum junction (V. J., Fig. 1). The source of irradiations consisted of a battery of two 200 watt incandescent (glass) bulbs run at 200 volts. The mode of observation of Δi was essentially similar to that described in Part I of this series (Mohanty and Kamath, this *Journal*, 1948, 25, 405). Data were obtained at different t between the room temperature, viz., 33° and 125° . In Table I, which represents but one typical set of observations, are shown the discharge current in dark i_d , that under irradiation i_L , the net Joshi effect $\Delta i (=i_d - i_L)$ and the relative effect $\% \Delta i (=100 \Delta i / i_d)$ for various V and at different t .

DISCUSSION

These results show that at the lowest temperature, viz., 33° , Δi increases slowly with V . At a higher t , on the other hand, the corresponding increase in Δi is comparatively rapid. Thus *e.g.*, Δi at 2.67 kV (r.m.s.) and 33° is 1.17. Increase of V to 3.2 kV enhances Δi to 1.54; a further rise in V to 4.27 kV raises Δi only to 1.75. At 75° , Δi increases from 1.06 at 2.67 kV to 2.03 at 4.27 kV. At 100° Δi attains a maximum (of 1.22) at 3.73 kV and decreases thereafter. The same behaviour is repeated at 125° . The relative effect $\% \Delta i$, however, decreases with V . At low t , there is at first a rapid and then a slow fall in $\% \Delta i$. Thus *e.g.*, at 33° , whilst an increase of V from 2.67 to 3.2 kV decreases $\% \Delta i$ from 29.3 to 20.2, a further rise of V to 4.27 kV reduces $\% \Delta i$ only to 17.1. It is significant that at higher t , the initial decrease with V of $\% \Delta i$ is not precipitous, the diminution being slow and uniform over the entire potential range investigated. Thus, at 75° , increase of V from 2.67 to 4.27 kV reduces $\% \Delta i$ from 18.4 to only 12.9.

Temperature increases markedly both i_d and i_L at constant V . Thus *e.g.*, i_d at 2.67 kV increases from 4.00 at 33° to 10.35 at 125° . Further, the rate of increase of i with t is initially small and becomes comparatively large at higher t . This behaviour is accentuated at higher applied V . Thus, whilst increase of t at 2.67 kV from 50°

to 75° enhances i_b from 4.58 to 5.75, an equal increase of t from 100° to 125° raises i_b from 7.14 to 10.35. At a higher V, e. g. 3.2 kV, i_b increases from 9.59 to 10.58 and from 12.49 to 21.35 over the above ranges of t .

TABLE I

Influence of temperature on the Joshi effect in oxygen.

$pO_2 = 331$ mm. (32°). Frequency of A. C. supply = 50 cyc./sec. Source of irradiation = Two 200 volt, 200 watt (glass) bulbs, 22 cm. from the ozoniser Detector = Vacuo-junction.

V in kilo-volts (r. m. s.)		T e m p e r a t u r e				
		33° .	50° .	75° .	100° .	125° .
2.67	i_b	4.00	4.58	5.75	7.14	10.35
	i_L	2.83	3.32	4.69	6.6	9.85
	Δi	1.17	1.26	1.06	0.54	0.50
	% Δi	29.3	27.5	18.4	7.6	4.8
2.93	i_b	6.45	7.68	8.78	9.7	15.46
	i_L	4.8	6.25	7.42	8.94	14.90
	Δi	1.45	1.43	1.36	0.76	0.56
	% Δi	23.2	18.6	15.5	7.8	3.6
3.2	i_b	7.62	9.59	10.58	12.49	21.35
	i_L	6.08	7.94	9.03	11.45	20.81
	Δi	1.54	1.65	1.55	1.04	0.54
	% Δi	20.2	17.2	14.7	8.3	2.5
3.47	i_b	8.37	10.86	12.33	14.70	
	i_L	6.78	9.00	10.58	13.60	
	Δi	1.59	1.86	1.75	1.1	
	% Δi	19.0	17.1	14.2	7.5	
3.73	i_b	9.00	11.92	13.64	16.77	
	i_L	7.35	9.9	11.79	15.55	
	Δi	1.65	2.02	1.85	1.22	
	% Δi	18.3	16.8	13.6	7.3	
4	i_b	9.75	12.84	14.90	18.84	
	i_L	8.00	10.73	12.92	17.69	
	Δi	1.75	2.11	1.98	1.15	
	% Δi	18	16.4	13.3	6.1	
4.27	i_b	10.24	13.75	15.78	20.52	
	i_L	8.49	11.62	13.75	19.64	
	Δi	1.75	2.13	2.03	0.88	
	% Δi	17.1	15.5	12.9	4.3	

The increase of i with t might be due, in part, to the enhanced mobility of ions brought about in consequence of the thermal break-down of ion-clusters. That such clusters are formed in oxygen appears plausible from the following theoretical considerations due to Hassé (*Phil. Mag.*, 1926, vii, 1, 139): The condition for cluster formation is that the potential energy of the molecule in contact with the ion must be greater than the average kinetic energy of relative motion :

$$\frac{(e-1)e^2}{8\pi n\sigma^4} / \frac{3}{2} RT = \frac{2}{3\lambda^2},$$

where ϵ is the dielectric constant of the gas ; e , the ion charge ; n , the number of molecules per unit volume ; σ , the distance of closest approach at a collision between ion and molecules and $\lambda^2 = 8\pi p \sigma^4 / (\epsilon - 1)e^2$. The ratio $\frac{2}{3}\lambda^2$ determines cluster formation. For $\lambda < 0.8165$, as obtains in oxygen, clusters occur.

Ozone is formed but to a small extent under the experimental conditions. Its thermal decomposition might contribute to the observed increase with t of i . This is to be anticipated from the results of Pinkus and Ruysen (*Bull. Soc. chim. Belg.*, 1928, **37**, 304) who observed that the decomposition of 10^{-6} to 10^{-7} g. mol. of ozone per second in a field of 845 volts/cm. produces currents of 10^{-11} to 10^{-12} amp. The temperature coefficient of the thermal decomposition of ozone is high, viz., 2.5 (Warburg, *Ann. Physik*, 1903, **9**, 1286 ; Clement, *ibid.*, 1904, **14**, 334 ; Chapman and Jones, *J. Chem. Soc.*, 1910, **97**, 2463).

Data regarding the dependence of ionic mobility K on t are scarce. Much of the earlier investigations were conducted under conditions which are far from satisfactory. Phillips (*Proc. Roy. Soc.*, 1906, **A**, **78**, 167) observed that the temperature variation of the mobility constant K , the mobility at the gas density ρ_0 at 0° and 760 mm. pressure, follows Sutherland's equation for viscosity. This, however, could not be substantiated by Kovacic (*Phys. Rev.*, 1910, **i**, **30**, 415) and Erikson (*ibid.*, 1914, **ii**, **8**, 151 ; 1915, **6**, 345). Later, Schilling (*Ann. Physik*, 1927, **83**, 23) tested the Sutherland law over a temperature range of 60° . Erikson's results which appear to be by far the best of the older work, covered a range from 400°A down to liquid-air temperatures. The mobility constant K altered but little, except at the lowest temperatures when it decreased by about 10%. Tyndall and Pearce (*Proc. Roy. Soc.*, 1935, **A**, **149**, 426) and Pearce (*ibid.*, 1936, **A**, **166**, 490) investigated the variation of K for N_2^+ in N_2 gas, and for Na^+ and Cs^+ in He. Owing to charge transference, results for N_2^+ in N_2 are of less significance. In the case of Na^+ and Cs^+ in He, it was found that the increase of K with t was more marked under conditions of constant pressure than under conditions of constant density. Any sensible change in the latter, however, is excluded by conditions (viz., a sealed Siemens' tube) under which the Joshi effect is determined. Increase of K will consequently be small and cannot account for the large current rise observed, e.g. about three-fold over $33^\circ\text{-}125^\circ$ at 3.2 kV.

The increase with t of the dielectric conductivity of glass is also a possible contributory factor. On the modern theory, the electrons in a solid dielectric just fill an energy band at the absolute zero. At any higher t some of the electrons are thermally excited into the next unoccupied band. The number of electrons excited is of the form $e^{-b/T}$; b is connected with the energy-step between the two bands. Since these electrons are free to move through the lattice, they produce an electrical conductivity whose temperature variation is also of the form $e^{-b/T}$ (Wilson, "Semiconductors and Metals", Cambridge Univ. Press, 1939). Experiment has shown (Whitehead, "Lectures on Dielectric Theory and Insulation", McGraw Hill, 1927) that the temperature variation of the final conductivity of glass obeys approximately the relation

$$I_t = I_0 e^{at},$$

where α is a constant. A corresponding change is observed in dielectric absorption of the substance.

Joshi (*Curr. Sci.*, 1947, **16**, 19) has shown that

$$i = V \left/ \frac{1}{jCw\sum f} + \frac{1}{1/Rg + jCg\sum f} \right.,$$

where j is the operator ($=\sqrt{-1}$), Cw , the combined capacity of the inner and outer electrode walls of the ozoniser; Cg , the capacitance due to the enclosed gas; Rg , the latter's ohmic resistance; $\sum f$, the frequency not only of the A. C. supply and its harmonics, but also those produced under the discharge. Increase of i at constant V would result from a like change in one or more of the quantities Cw , Cg , $1/Rg$ and $\sum f$. The probable mechanism leading to an increase with t of the ohmic conductance $1/Rg$ (which depends on the number and velocity of the ions) has been considered (*vide supra*). Temperature increases appreciably the dielectric constant of glass (Gray and Dobbie, *Proc. Roy. Soc.*, 1898, **A**, **63**, 38; 1900, **A**, **67**, 197), and hence also Cw . The dielectric constant of the gas (and hence Cg), on the other hand, decreases. This diminution is, however, small on account of the inappreciable reduction in the density of the enclosed oxygen. Besides, an increase in $\sum f$ with t is not unlikely.

The 'threshold potential' V_m (at which i increases markedly with the applied V), obtained by extrapolation of the $V-i_0$ curves, increases with t up to 50° and decreases thereafter. This is evident from the following results.

t	33°	50°	75°	100°	125°
V_m (in kilo-volts)	... 2.31	2.37	2.31	2.19	2.16
% Variation from 33°	... —	+2.6	0.00	-5.2	-6.5

Opinion is divided on the dependence of electrical break-down strength of solid dielectrics on temperature. According to Inge, Semenoff and Walther (*Archiv Elektrotechnik*, 1926, **17**, 433), the break-down strength is independent of temperature. Buehl and von Hippel (*Phys. Rev.*, 1939, **58**, 941) found, on the other hand, that for pure ionic crystals, the electronic break-down strength increases with t to a maximum and then decreases. The break-down path in these cases depends on the crystallographic orientation (von Hippel, *Trans. Faraday Soc.*, 1946, **42 A**, 78).

The net effect Δi at constant V increases with t up to 50° and then decreases. Thus *e. g.*, Δi at 3.2 kV and 33° is 1.54; it is 1.65 at 50° and 1.55 at 75° . Above 3.07 kV, Δi at 75° is larger than that at 33° ; below this potential, the reverse is the case. At 100° and 125° , Δi is markedly reduced, being only 1.04 and 0.54 respectively at 3.2 kV. The relative effect $\% \Delta i$ decreases progressively with t . Thus, at the above potential it is 20.2 at 33° and diminishes to 2.5 at 125° .

According to Joshi (*Proc. Indian Sci. Cong.*, 1946, Part III, *Phys. Sec.*, Abst. No. 26; 1947, Part III, *Phys. Sec.*, Abst. No. 25; *Curr. Sci.*, 1946, **15**, 281; 1947, **16**, 19), the formation on the excited electrodes of a boundary layer derived, in part; from a

wall-adsorption of ions and neutral molecules in the discharge space, is primary to Δi . Electrons released from this layer on irradiation are captured by the electronegative gas elements forming slow moving negative ions which reduce i by a space-charge effect. Heating would cause desorption and depolarization of the ions and the other particles constituting the electrode layer. Decrease in Δi with t , as observed, is therefore to be anticipated. It is also known (Huges and Dubridge, "Photo-electric Phenomena", McGraw Hill, 1932) that whilst photo-electron emission from pure metals increases with temperature, that from a surface film of a certain critical thickness deposited on a metal is reduced due to heating. At higher temperatures, the formation of negative ions may be inhibited leading to a decrease in Δi .

The author's thanks are due to Professor S. S. Joshi for having suggested the problem, and for his instructive advice and kind encouragement during the work.

DEPARTMENT OF CHEMISTRY,
BENARES HINDU UNIVERSITY.

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COMPLEX COMPOUNDS OF BIGUANIDE WITH BIVALENT METALS.
PART IX. AMPHOLYTIC INNER-METALLIC COPPER AND
NICKEL COMPLEXES WITH NAPHTHYLBIGUANIDE
o-SULPHONIC ACID AND PHENYLBIGUANIDE
p-SULPHONIC ACID, AND ITS SALTS

By PRIYADARANJAN RÂY AND RABINDRA KUMAR DUTT

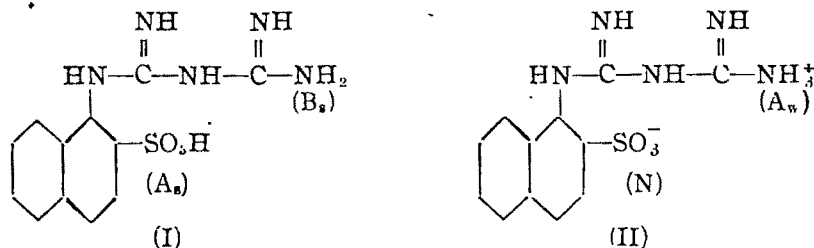
Naphthylbiguanide *o*-sulphonic acid has been prepared from α -naphthylamine *o*-sulphonic acid and dicyandiamide. Ampholytic inner-complexes of α -naphthylbiguanide *o*-sulphonic acid with copper and nickel have been prepared and their properties studied. These have been described as belonging to the class of inner-metallic complexes of the fourth order. They are all insoluble like the inner complexes of the first order. From these ampholytic complexes the corresponding soluble alkali-metal salts have been prepared and studied. The biguanide metal complexes behave as anions in these salts. Similar alkali salts have been prepared also of ampholytic copper and nickel complexes of phenylbiguanide *p*-sulphonic acid along with their corresponding cobaltic *tris*biguanide salts. A green modification of copper phenylbiguanide *p*-sulphonic acid has been obtained in addition to the red form previously described by Rây and Siddhanta. The two forms are represented as *cis-trans* isomers. Both give the same magnetic moment value of 1.85 Bohr, expected for a planar penetration complex of copper.

In previous parts of this series of investigation Rây and his co-workers have shown that biguanide and its derivatives combine with bi- and trivalent metallic elements like Cu, Ni, Pd, Co and Cr to form inner-metallic complexes of a new type, as these are not necessarily insoluble and non-electrolyte like the well-known inner complex salts formed by glycine, dimethylglyoxime, 8-oxyquinoline, etc. with metallic elements. The free amino groups in these compounds share the properties of a weak base and readily combine with acids and water to form salts and basic hydroxides respectively. To these the name inner-metallic complexes of the third order may be given. For, complexes in which the primary valencies of the central atom are completely satisfied by co-ordination with chelate groups and which become insoluble and non-electrolyte as mentioned above, are termed, according to Werner, inner-metallic complexes of the first order; while those in which the primary valencies of the central atom are not fully saturated by the co-ordinating chelate groups and which can therefore behave as an electrolyte, were named inner-metallic complexes of the second order by Werner. Examples of this latter type are furnished by acetylacetonates of silicon, boron, cobalt (ous), etc., as shown hereafter.

Rây and Siddhanta (*J. Indian Chem. Soc.*, 1943, 20, 250) have, however, prepared biguanide complexes which are completely insoluble and non-electrolyte like the inner-metallic complexes of the first order. Phenylbiguanide *p*-sulphonic acid combines with nickel, copper and cobalt to form such compounds. The basic character of the free amino group in these complexes is more than completely neutralised by the sulphonic acid group within the same molecule. The complex therefore like the co-ordinating molecule, phenylbiguanide *p*-sulphonic acid itself, behaves as an amphoteric electrolyte or zwitter ion. In order to distinguish these complexes from those of the inner complexes of the first order, we may call them inner-metallic complexes of the fourth order.

α -Naphthylbiguanide *o*-sulphonic acid, a higher homologue of phenylbiguanide *p*-sulphonic acid, has been prepared and a study of its complex copper and nickel compounds included here.

This reagent, like its analogue phenylbiguanide *p*-sulphonic acid, exists in the form of zwitter ion (II) as represented below :



(A_s = strong acid, B_s = strong base, A_w = weak acid, N = neutral). The substance is, therefore, expected to be practically insoluble in water, due to internal salt formation which has actually been found to be the case. It is, however, soluble in both acids and alkalis.

The complex copper and nickel compounds of naphthylbiguanide *o*-sulphonic acid like the corresponding complexes of phenylbiguanide *p*-sulphonic acid are quite insoluble in water resembling the inner complexes of the first order and behaving as ampholytes. They are soluble in alkalis. It is thus found that co-ordination with copper and nickel enhances the acid character of the ampholyte. This has made possible the preparation of the alkali salts of the ampholytic complexes. Acids, on the other hand, lead to the decomposition of these complexes. The phenylbiguanide *p*-sulphonic acid complexes also behave in the same way. A quite stable, bright red cobaltous complex of phenylbiguanide *p*-sulphonic acid, resembling vermilion, has also been prepared. The alkali salts of phenylbiguanide *p*-sulphonic acid complexes are comparatively more soluble and stable than the salts of the corresponding naphthyl complexes. From these alkali salts compounds of the composition, [Co (BigH)₃]₂ [Ni (PhBig. SO₃)₂]₃ and the corresponding compound of copper in place of nickel have been obtained. BigH represents a biguanide molecule. These salts of the metalbiguanide ampholytic complexes, with the latter forming an anion, belong, therefore, like the normal biguanide complexes to the class of inner-metallic complexes of the third order.

The inner-metallic complexes can thus be classified into four different groups.

The inner-metallic complexes of the first order comprise all those which are insoluble non-electrolyte with no free salt-forming radicals in the molecule, e.g., nickel dimethylglyoxime, copper glycine, cobaltic acetylacetonate, etc.

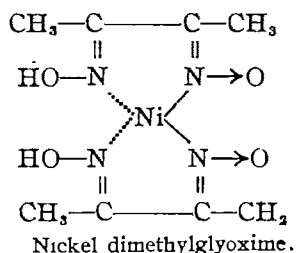
Those of the second order are represented by complexes in which the primary valency of the central atom is either incompletely satisfied or more than satisfied by the co-ordinating groups. These can, therefore, behave as electrolytes, e.g., silicon acetylacetonate chloride, sodium cobaltous *tris*-acetylacetonate, etc.

Inner complexes of the third order contain a free salt-forming group or radical in the co-ordinated molecules. This makes them behave as electrolytes, e.g., metalbiguanide salts.

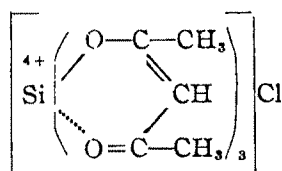
Those of the fourth order are represented by ampholytic complexes, which are insoluble in water but dissolve in alkalis giving rise to the formation of inner complexes of the third order, e.g., inner-metallic complexes with phenyl or naphthylbiguanide sulphonic acid.

These are illustrated by the following configurations.

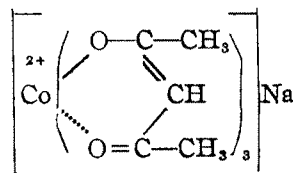
1. Inner-metallic complex of the first order :



2. Inner-metallic complex of the second order :

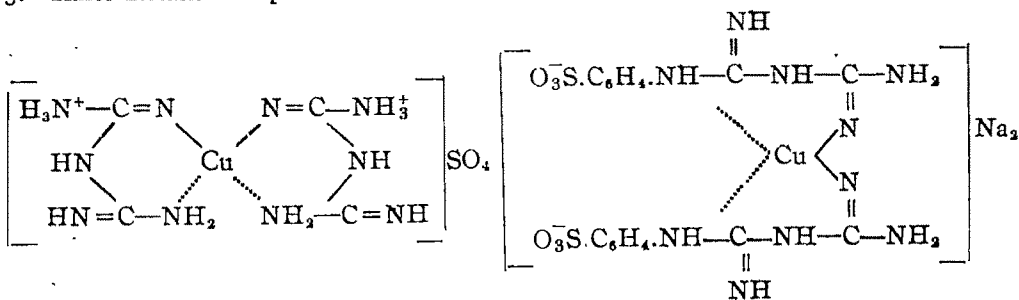


Silicon acetylacetonate chloride

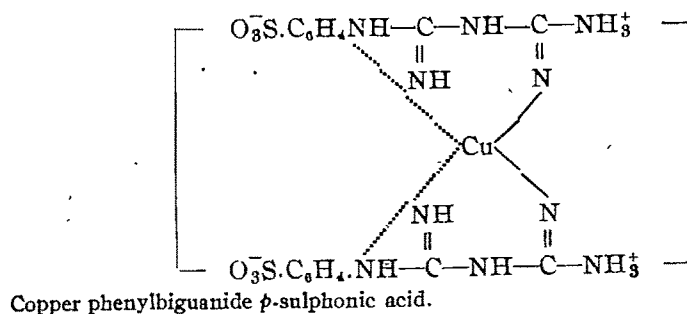


Sodium cobaltous acetylacetonate.

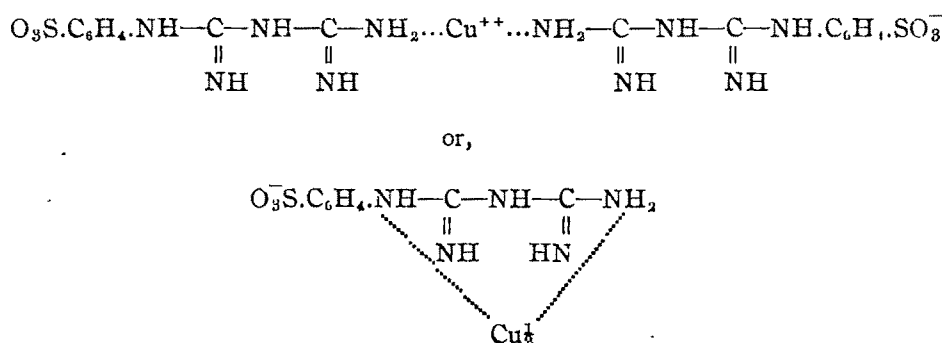
3. Inner-metallic complex of the third order .



4. Inner-metallic complex of the fourth order :



A green modification of the copper phenylbiguanide *p*-sulphonic acid has been obtained in addition to the reddish violet variety previously described by Rây and Siddhanta (*loc. cit.*). The nature of the product *vis a vis* that of its red modification is not quite clear. The possibility of cis-trans isomerism might be suggested, though instances of such isomerism in the case of copper are rather rare (cf. Rây and Chakrabarty, *J. Indian Chem. Soc.*, 1941, 21 609). The red modification changes to the green form slowly in presence of strong ammonia but rapidly on heating; a long time is, however, necessary for a complete conversion. This difference in colour may also arise from a difference in particle size or polymerization. A third possible explanation might be based on the assumption that the green form represents not an inner-metallic complex as described above, but only an associated complex of the type shown below:



This resembles the copper salt of sulphanilic acid or copper ethylenediamine complexes, the latter configuration having the possibility of occurring in cis-trans isomeric forms. But in view of the strong bifunctional character of the biguanide group giving rise to the inner-metallic complexes, neither of these configurations would represent a stable state. The green variety, once formed, is, however, quite stable and is not affected even by boiling water. The two forms may, therefore, be regarded as cis-trans isomers of the planar copper complex, the less stable reddish violet modification representing the *cis* configuration.

Evidences in support of the planar configuration for copper complexes are derived not only from the classical methods of stereochemistry but also from a substantial mass of physical data, specially relating to the X-ray measurements of the crystalline salts. Thus the planar configuration has been found for the cupric derivatives of β -diketones (Cox and Webster, *J. Chem. Soc.*, 1935, 731), for copper phthalocyanin complex (Robertson, *ibid.*, 1935, 615), for dipyrindine cupric chloride (Cox, Sharatt, Wardlaw and Webster, *ibid.*, 1936, 129).

Though the nickel phenylbiguanide has been found by Rây and Chakrabarty (*J. Indian Chem. Soc.*, 1941, 19 609) in three different modifications, the corresponding ampholytic complexes of phenylbiguanide and naphthylbiguanide sulphonic acids have, however, been obtained only in one form. On the other hand, the sodium salt of nickel naphthylbiguanide *o*-sulphonic acid has been obtained in two modifications, red (stable at low temperature) and yellow. They might as well be related to each other as cis-trans isomers, the yellow stable form representing the *trans* variety. It might as

well be due to polymorphism as already referred to. Occurrence of cis-trans isomerism in the case of planar nickel complexes has been proved by several workers (cf. Sugden, *J. Chem. Soc.*, 1932, 246; Cox, Wardlaw, *et al.*, *ibid.*, 1935, 459, 1473).

The cobaltous phenylbiguanide *p*-sulphonic acid, described here, differs, however, considerably in its physical and chemical properties from the similar cobaltous complexes with simple biguanide and ethylenedibiguanide previously described by Rây and Ghosh (this *Journal*, 1943, 21, 292, 323). Whereas the latter compounds are true inner-metallic complexes of the third order, as their colour and magnetic moment suggest (2.66 Bohr), the cobaltous phenylbiguanide *p*-sulphonic acid, on the other hand, is highly red and gives a moment value (5 Bohr) equal to that for a simple cobaltous ion. Besides, while the yellow cobaltous biguanide complexes are rather unstable and are readily oxidized to the cobaltic state in the presence of moist air, the red cobaltous phenylbiguanide *p*-sulphonic acid is quite stable in air and water. Only by the action alkali solution it changes its colour to yellow with rapid oxidation to the complex cobaltic state, forming the alkali salt of cobaltic phenylbiguanide *p*-sulphonic acid. From these considerations it may be concluded that the red stable cobaltous phenylbiguanide *p*-sulphonic acid is probably an associated complex of the type discussed above in connection with the green copper complex and that, in presence of alkali, it changes to the yellow inner-metallic complex of the fourth order, which could not, however, be isolated on account of its great instability.

EXPERIMENTAL

Naphthylbiguanide o-Sulphonic Acid.—A mixture of sodium α -naphthylamine *o*-sulphonic acid (6 g.), dicyandiamide (2 g.), 70% HCl (7.2 c.c.) and water (60 c.c.) was heated for about an hour and a half with a reflux condenser, when white crystals of the substance separated gradually. These were collected and filtered. The product was purified by dissolving it in hot dilute hydrochloric acid and then reprecipitating by the addition of dilute ammonia. This was washed with water and dried in air. (Found: N, 22.88. $\text{HO}_3\text{S.C}_{10}\text{H}_8\text{.C}_2\text{N}_5\text{H}_8$ requires N, 22.87 per cent).

The substance forms white fine powder, insoluble in water. It dissolves both in mineral acids and caustic alkalis, and is also sparingly soluble in ammonia.

Copper Naphthylbiguanide o-Sulphonic Acid.—Naphthylbiguanide *o*-sulphonic acid (2 g.) was dissolved in dilute HCl. A solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was then slowly added to it. The mixture was afterwards treated with dilute ammonia with constant stirring, when a blue-violet precipitate gradually separated out. This was purified by dissolving it in dilute HCl and then reprecipitating with dilute ammonia. The product was washed first with water, then with alcohol and finally dried in air. {Found: N, 20.82; Cu, 9.45. $(\text{HO}_3\text{S.Nap.Big})_2\text{Cu}$ requires N, 20.78; Cu, 9.42 per cent} where $\text{HO}_3\text{S.Nap.BigH}$ = a molecule of naphthylbiguanide sulphonic acid.

The substance forms a blue-violet powder, insoluble in water and dilute ammonia. It dissolves in caustic alkalis with formation of a permanganate-red colour and is decomposed by mineral acids.

2. *Potassium Copper Naphthylbiguanide o-Sulphonate*.—Copper naphthylbiguanide *o*-sulphonic acid (3 g.) was dissolved in a moderately cold solution of KOH. On concentrating and cooling the solution violet crystals separated from it. These were filtered and washed with absolute alcohol. The substance was recrystallised by dissolving in the least quantity of warm water containing a little dilute KOH solution and then cooling the mixture in ice. The crystals were filtered, washed several times with alcohol and finally dried in air {Found: N, 16.98; Cu, 7.73; K, 9.61. $K_2[Cu(SO_3.NapBig)_2].4H_2O$ requires N, 17.04; Cu, 7.74; K, 9.50 per cent }.

The substance partially hydrolyses in water with formation of the insoluble copper complex.

3. *Sodium Copper Naphthylbiguanide o-Sulphonate*.—A moderately concentrated solution of sodium hydroxide was added to moist copper naphthylbiguanide *o*-sulphonic acid, drop by drop, till the latter dissolved. The solution was concentrated on the water-bath and then cooled in ice, when blue-violet crystals of the substance separated from the solution. These were filtered and washed with 70% alcohol containing a little NaOH and finally with absolute alcohol. The product was purified by recrystallisation as described in the previous case. {Found: N, 17.38, Cu, 7.90; Na, 5.65. $Na_2[Cu(SO_3.NapBig)_2].5H_2O$ requires N, 17.33; Cu, 7.87; Na, 5.69 per cent }.

It resembles the potassium salt in properties.

4. *Nickel Naphthylbiguanide o-Sulphonate*.—Naphthylbiguanide *o*-sulphonic acid (3 g.) was dissolved in dilute HCl. To this a solution of $NiSO_4.6H_2O$ (1 g.) was added and the mixture was made alkaline by the addition of dilute ammonia. The resulting rose-coloured precipitate was filtered and washed with water. The product was purified by dissolving it in dilute HCl and then reprecipitating by adding an excess of dilute ammonia. The substance was washed and dried as usual. {Found: N, 18.47; Ni, 7.73. $Ni(HO_3S.NapBig)_2.5H_2O$ requires N, 18.45; Ni, 7.73 per cent }.

The substance is insoluble in water and dilute ammonia, but dissolves in caustic alkalis to a red solution. It is decomposed by mineral acids.

5. *Potassium Nickel Naphthylbiguanide o-Sulphonic Acid*.—Nickel naphthylbiguanide *o*-sulphonic acid was dissolved in a moderately concentrated KOH solution. This on concentration on the water-bath and subsequent cooling, gave beautiful yellow crystals of the potassium salt. The product was recrystallized from hot water containing a little KOH solution. The crystals were washed and dried as usual. {Found: N, 17.92; Ni, 7.47; K, 10.0. $K_2[Ni(SO_3.NapBig)_2].2H_2O$ requires N, 17.93; Ni, 7.51; K, 9.99 per cent }.

The substance is soluble in water with partial hydrolysis and is decomposed by mineral acids.

6. *Sodium Nickel Naphthylbiguanide o-Sulphonate (yellow)*—This was prepared like the potassium salt by using NaOH in place of KOH. {Found: N, 16.56; Ni, 6.95; Na, 5.46. $Na_2[(O_3S.NapBig)_2Ni].7H_2O$ requires N, 16.57; Ni, 6.99; Na, 5.46 per cent }.

Its properties resemble those of the potassium salt. It forms beautiful yellow crystals.

7. *Sodium Naphthylbiguanide o-Sulphonate (red).*—When nickel naphthylbiguanide was dissolved in cold dilute NaOH solution and the latter was allowed to crystallize in vacuum over H_2SO_4 , red coloured crystals of the salt separated from it. These were washed and dried as usual. {Found : N, 16.60 ; Ni, 6.92 ; Na, 5.46. $\text{Na}_2[\text{Ni}(\text{O}_3\text{S. NapBig})_2] \cdot 7\text{H}_2\text{O}$ requires N, 16.57 ; Ni, 6.99 ; Na, 5.48 per cent}.

8. *Copper Phenylbiguanide p-Sulphonic Acid (green).*—Phenylbiguanide *p*-sulphonic acid (3 g.) was dissolved in hot concentrated ammonia. This was then treated with a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1 g.) with constant stirring, when beautiful green crystals of the compound gradually separated out. The product was purified by dissolving it in acid and then reprecipitating from the solution by the addition of hot ammonia. {Found : N, 23.56 ; Cu, 10.68. $\text{Cu}(\text{HO}_3\text{S. PhBig})_2 \cdot 5\text{H}_2\text{O}$ requires N, 23.79 ; Cu, 10.73. per cent} where PhBigH = a molecule of phenylbiguanide.

Rây and Siddhanta (*loc. cit.*) have described a red-violet variety of the compound. Both the red-violet and the green forms are mutually convertible. Both give almost the same magnetic moment value. They both dissolve in alkali to give the same red solution from which the red-violet form separates by neutralisation with acid in the cold. The red form changes to the green variety on warming with ammonia solution.

Magnetic Measurements.

	$t = 32^\circ$	
Green modification :	$\chi_g = 1.84 \times 10^{-6}$, $\chi_A = 1384 \times 10^{-6}$,	$\chi_M = 1109 \times 10^{-6}$, $\mu_B = 1.84$.
Red-violet modification	$\chi_g = 1.90 \times 10^{-6}$, $\chi_A = 1397 \times 10^{-6}$,	$\chi_M = 1128 \times 10^{-6}$, $\mu_B = 1.85$.

9. *Potassium Copper Phenylbiguanide p-Sulphonate.*—Copper phenylbiguanide *p*-sulphonic acid was dissolved in strong KOH solution. After concentration on the water-bath alcohol was added to the cooled mixture. The resulting rose-coloured precipitate was purified by dissolving it in the least amount of water and then reprecipitating with alcohol. The product was washed and dried as usual. {Found : N, 20.83 ; Cu, 9.60 ; K, 12.0. $\text{K}_2[\text{Cu}(\text{O}_3\text{S. PhBig})_2] \cdot \text{H}_2\text{O}$ requires N, 20.92 ; Cu, 9.59 ; K, 11.82 per cent}.

10. *Sodium copper phenylbiguanide p-sulphonate* was prepared like the potassium salt from the copper phenylbiguanide *p*-sulphonic acid and caustic soda solution. {Found : N, 20.98 ; Cu, 9.54 ; Na, 6.97. $\text{Na}_2[\text{Cu}(\text{O}_3\text{S. PhBig})_2] \cdot 2.5\text{H}_2\text{O}$ requires N, 21.06 ; Cu, 9.56 ; Na, 6.92 per cent}.

11. *Potassium nickel phenylbiguanide p-sulphonate* was prepared by dissolving nickel phenylbiguanide *p*-sulphonic acid in moderately concentrated solution of KOH. The solution, after concentration on the water-bath, was cooled in ice when beautiful yellow crystals of the compound separated out. These were recrystallized from warm water. The product was washed and dried as usual. {Found : N, 19.75 ; Ni, 8.26 ; K, 11.03. $\text{K}_2[\text{Ni}(\text{O}_3\text{S. PhBig})_2] \cdot 3.5\text{H}_2\text{O}$ requires N, 19.75 ; Ni, 8.27 ; K, 10.90 per cent}.

12. *Sodium nickel phenylbiguanide p-sulphonate* was prepared in the same way as the previous compound using NaOH in place of KOH. It resembles the potassium salt in properties. {Found : N, 20.89 ; Ni, 8.75 ; Na, 6.90. $\text{Na}_2[\text{Ni}(\text{O}_3\text{S}.\text{PhBig})_2].3\text{H}_2\text{O}$ requires N, 20.87 ; Ni, 8.75 ; Na, 6.85 per cent}.

13. *Cobaltous Phenylbiguanide p-Sulphonic Acid*.—A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1 g.) was added to an ammoniacal solution of phenylbiguanide *p*-sulphonic acid (3.5 g.) with constant stirring when the compound separated out in beautiful red crystals. These were washed and dried as usual. {Found : N, 23.95 ; Co, 10.15. $\text{Co}(\text{HO}_3\text{S}.\text{PhBig})_2.5\text{H}_2\text{O}$ requires N, 24.10 ; Co, 10.17 per cent}.

The substance resembles vermilion in colour and dissolves in aqueous alkali to form a yellow solution which rapidly turns red from oxidation. It is quite stable and strongly paramagnetic.

$$\chi_g = 15.0 \times 10^{-6}, \quad \chi_M = 9915 \times 10^{-6}, \quad \chi_A = 10235 \times 10^{-6}, \quad \mu_B = 4.97. \quad t = 27^\circ.$$

14. *Cobaltic tris-biguanidinium copper phenylbiguanide p-sulphonate* was obtained as a light rose precipitate by adding a solution of cobaltic *tris*-biguanide chloride to a concentrated solution of potassium copper phenylbiguanide *p*-sulphonate. The product was washed and dried as usual. {Found : N, 32.75 ; Cu, 7.46 ; Co, 4.66. $[\text{Co}(\text{BigH})_3]_2 [\text{Cu}(\text{O}_3\text{S}.\text{PhBig})_2]_3.6\text{H}_2\text{O}$ requires N, 32.94 ; Cu, 7.48 ; Co, 4.63 per cent}.

15. *Cobaltic tris-biguanidinium nickel phenylbiguanide p-sulphonate* was obtained as an orange-coloured precipitate from cobaltic *tris*-biguanide chloride and potassium nickel phenylbiguanide sulphonate. {Found : N, 31.62 ; Ni, 6.61 ; Co, 4.45 ; $[\text{Co}(\text{BigH})_3]_2 [\text{Ni}(\text{O}_3\text{S}.\text{PhBig})_2]_3.12.5\text{H}_2\text{O}$ requires N, 31.60 ; Ni, 6.67 ; Co, 4.46 per cent}.

INORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA.

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PHYSICO-CHEMICAL STUDIES IN THE FORMATION OF COMPLEX
STANNIOXALATES. PART I. CONDUCTOMETRIC STUDY OF
THE $\text{Sn}(\text{OH})_4\text{--H}_2\text{C}_2\text{O}_4$ SYSTEM

BY ARUN K. DEY AND A. K. BHATTACHARYA

The complex formation between stannic tin and oxalic acid has been studied by the electrical conductivity method. From the curves, evidence has been obtained for the existence of the compounds: $\text{Sn}(\text{C}_2\text{O}_4)_2$ and $\text{H}_4\text{Sn}(\text{C}_2\text{O}_4)_4$

In several publications (Dey and Bhattacharya, *Curr. Sci.*, 1945, 14, 69; Dey, *Univ. Allahabad Studies*, 1946, 22, 7) it has been shown that the inhibition of the precipitation of stannic sulphide in presence of certain organic acids is due to complex formation between stannic tin and the carboxylic ion. The extent of such an inhibition has been quantitatively studied using different quantities of oxalic acid, oxalates (Dey and Bhattacharya, *Proc. Nat. Acad. Sci. India*, 1946, 15, 86) and soluble tartrates (Dey, *ibid.*, 1947, 16, 27). The present study has been undertaken with a view to elucidating the composition of the complexes formed in a mixture of solutions of stannic tin and oxalates and this paper records the experimental results obtained by the conductometric study of stannic hydroxide-oxalic acid system.

EXPERIMENTAL

Since a solution of stannic chloride was made in hydrochloric acid to prevent hydrolysis, the solution was extremely conducting. With the experimental arrangement at our disposal it was not possible to detect minute changes in conductivity. Therefore it was thought proper to use a suspension of stannic hydroxide instead of stannic chloride solution. A concentrated solution of stannic chloride was prepared by dissolving about 50 g. of Schuchardt's stannic chloride crystals in water, acidulated with hydrochloric acid. Stannic hydroxide was precipitated from this solution by the gradual addition of a slight excess of a diluted solution of Merck's ammonia. The precipitate was washed with cold water and finally filtered through a Buchner's flask and washed thoroughly till free from electrolytes. It was then transferred to a Jena bottle, made up to a litre and shaken vigorously to obtain a homogeneous suspension. Ten c.c. of this suspension were delivered in several silica crucibles, evaporated and finally heated strongly till the weights of the residue in all the cases were constant, ensuring the homogeneity of the suspension and also the concentration.

For conductivity measurements a high degree of accuracy was maintained. Rowland's roller bridge was used and the induction coil was actuated by a lead accumulator giving not less than 2 volts. The conductivity cell was kept immersed in a thermostat maintaining a constant temperature of $20 \pm 0.1^\circ$.

In determining the cell constant, account was taken for the disuniformity of the bridge wire and the bridge was calibrated with respect to the cell constant. The method for the calibration was the modified method of Wark (*J. Phys. Chem.*, 1930, 34, 885)

as adopted by Ghosh and Jha (*J. Indian Chem. Soc.*, 1945, **22**, 275). In all calculations the value of the calibration constant was used for the cell constant at various positions of the bridge wire. For the values for cell constant obtained at different positions of the bridge wire a graph was plotted and the value for the constant at any intermediate position on the wire was read from the calibration curve.

Standard solutions of oxalic acid were prepared using 'AnalaR' sample and double distilled conductivity water. Specific conductance values for different concentrations of oxalic acid solutions were determined. The values are given in Table I.

TABLE I

Electrical conductivity of oxalic acid at different dilutions.

Conc.	...	M/80	M/72	M/64	M/56	M/48	M/40	M/36	M/32	M/28
Conductivity (in 10^{-3} mhos)	..	3.833	4.146	4.704	5.186	6.011	6.982	7.554	8.265	9.343
Conc.	...	M/24	M/20	M/16	M/12	M/10	M/8	M/6	M/4	
Conductivity (in 10^{-3} mhos)	...	10.416	12.116	13.526	16.653	19.801	23.002	27.655	38.075	

Now, to a measured volume of the homogeneous stannic hydroxide suspension was added an equal volume of oxalic acid solution and the mixture was maintained at 20° for half an hour with occasional stirring. Several such mixtures were taken using different concentration of oxalic acid. After keeping at constant temperature, the conductivity of the supernatant liquids (where dissolution was not complete) or the clear solutions was determined. The results are presented in the following table.

TABLE II

Electrical conductivity of mixtures of stannic hydroxide and oxalic acid of various compositions.

Conc. of stannic hydroxide suspension = 0.8969 g. mol./litre.

Final conc. of oxalic acid in the mixture.	Ratio. total Sn : oxalic acid in the system.	Obs. conductivity of the mixture in 10^{-3} mhos.	Final conc. of oxalic acid in the mixture.	Ratio of total Sn : oxalic acid in the system.	Obs conductivity of the mixture in 10^{-3} mhos.
M/80	1 : 0.28	1.043	M/24	1 : 0.92	7.763
M/72	1 : 0.32	1.244	M/20	1 : 1.12	9.524
M/64	1 : 0.36	1.624	M/16	1 : 1.40	12.444
M/56	1 : 0.40	2.024	M/12	1 : 1.86	15.518
M/48	1 : 0.46	2.654	M/10	1 : 2.24	19.122
M/40	1 : 0.56	3.682	M/8	1 : 2.78	23.373
M/36	1 : 0.62	4.362	M/6	1 : 3.72	29.680
M/32	1 : 0.70	5.052	M/4	1 : 5.58	37.418
M/28	1 : 0.80	6.163			

DISCUSSION

The electrical conductivity results, as recorded in the preceding tables, are able to identify complex ions in a solution of stannic ions in oxalic acid, as found from the fact that the specific conductivity of the mixtures are not equal to the sum of those for the constituents. In the table below the percentage change in conductivity due to complex formation has been shown. In the cases where small quantities of oxalic acid are used, the hydroxide does not dissolve. So the ratio $\text{Sn} : \text{C}_2\text{O}_4$ refers to the total Sn in the system. These data are incorporated to give an idea of adsorption of oxalic acid by the hydroxide.

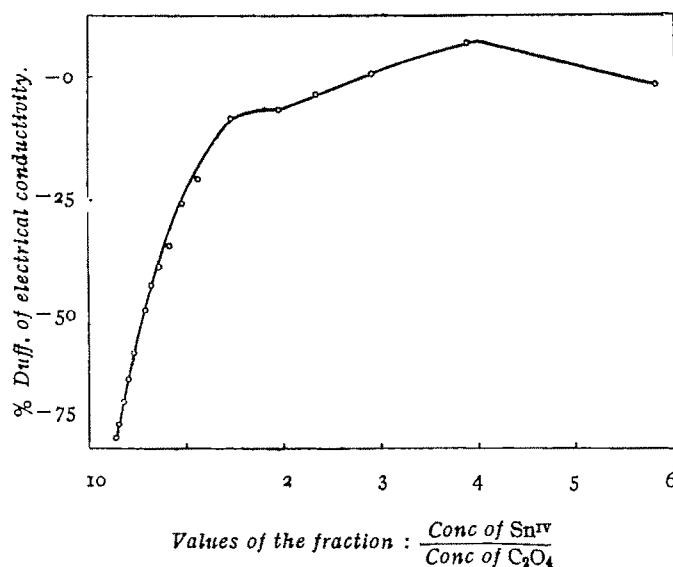
TABLE III

Changes in conductivity due to complex formation.

Ratio $\text{Sn}^{IV} : \text{C}_2\text{O}_4^{--}$	Conductivity of oxalic acid in 10^{-3} mhos.	Conductivity of mixture in 10^{-3} mhos.	Difference in 10^{-3} mhos.	Percentage difference.
1 : 0.28	3.833	1.043	-2.790	-72.78
1 : 0.32	4.146	1.244	-2.902	-69.98
1 : 0.36	4.704	1.624	-3.080	-65.46
1 : 0.40	5.186	2.024	-3.162	-60.98
1 : 0.46	6.011	2.654	-3.357	-55.84
1 : 0.56	6.982	3.682	-3.300	-47.26
1 : 0.62	7.554	4.362	-3.192	-42.25
1 : 0.70	8.265	5.052	-3.213	-38.86
1 : 0.80	9.343	6.163	-3.180	-34.07
1 : 0.92	10.416	7.763	-2.653	-25.45
1 : 1.12	12.116	9.524	-2.592	-20.57
1 : 1.40	13.525	12.444	-1.081	-7.99
1 : 1.86	16.653	15.518	-1.135	-6.80
1 : 2.24	19.801	19.122	-0.679	-3.43
1 : 2.78	23.002	23.373	+0.371	+1.13
1 : 3.72	27.655	29.680	+2.025	+7.32
1 : 5.58	38.075	37.418	-0.657	-1.73

A perusal of the graph showing the change in percentage difference of conductivity with the composition of the mixture will make it clear that with lower amounts of oxalic acid there is a marked decrease in electrical conductivity. It has been found by performing some experiments that stannic hydroxide, when freshly precipitated, adsorbs oxalic acid to an appreciable extent. Further, it is well known that oxalic acid peptises stannic hydroxide to the colloidal state. Dhar and co-workers (various papers in *J. Phys. Chem.*, 1925-30) have repeatedly emphasized that adsorption often precedes a chemical reaction and therefore it is evident that prior to complex formation a colloid is apt to form by the action of oxalic acid on stannic hydroxide. Hence, the conductivity values for mixtures naturally are diminished markedly when adsorption is predominant,

FIG. 1

 $\text{Sn(OH)}_4\text{-H}_2\text{C}_2\text{O}_4$ system.

especially when lower concentrations of oxalic acid have been used. The difference now goes on diminishing as the quantity of oxalic acid is increased : this occurs with progressive formation of the compounds. The first break in the curve occurs at the ratio $\text{Sn}^{IV} : \text{C}_2\text{O}_4 = 1:2$, i.e. the compound $\text{Sn(C}_2\text{O}_4)_2$ is formed at this stage. The second break, a maximum in the curve, shows the existence of the complex compound $\text{H}_4\text{Sn(C}_2\text{O}_4)_4$. These results therefore lead us to the conclusion that besides the formation of normal stannic oxalate, only one compound, a complex one, is formed by the reaction between stannic hydroxide and oxalic acid. It is interesting to observe that various earlier workers (vide Dey and Bhattacharya, *loc. cit.*) isolated complex compounds by crystallisation of mixtures of stannic chloride and organic acids. The compositions reached by them by chemical analysis seem to be those for double salts or adsorption compounds rather than true complexes. We are therefore of opinion, that in addition to ordinary chemical methods, physico-chemical methods must be adopted in order to get an idea of the composition of complex compounds.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SAUGOR,
SAUGOR, C.P.

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APPLICATION OF MIXTURE LAW TO RHEOCHOR. PART II

By S. W. SUBNIS, W. V. BHAGWAT AND R. B. KANUGO

The mixture law for the rheochors of acetic acid, acetone, ethyl alcohol and methyl alcohol in water has been applied and it is found to break down for all except acetic acid. However, with increase in concentration of the solutes R_x approaches R_{obs} so that by extrapolation ($x=1$) it is possible to calculate the value of the rheochor of the solute.

In Part I of this series of papers (this *Journal*, 1948, 28, 164) some results for the application of mixture law to rheochor of associated solutes in associated solvents were recorded. The work has been extended to acetic acid, acetone, ethyl alcohol and methyl alcohol with water as a solvent. In case of parachor Hammick and Andrew (*J. Chem. Soc.*, 1929, 759) have remarked that water shows anomalous behaviour. We have tried therefore in this communication to see how far the same observation applies to rheochor. The results are recorded in the following tables.

TABLE I

Acetic acid in water.

$R_{calc.}$ for acetic acid = 75.3.

x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x
Temp. = 30°.					
0.0000	0.9957	8.004	18.0000	23.45	—
0.0446	1.0142	9.936	19.8732	26.11	83.40
0.2111	1.0481	15.456	26.8662	36.08	83.32
0.2322	1.0508	16.056	27.7524	37.39	83.41
0.4251	1.0610	19.616	35.8542	49.01	83.60
0.6452	1.0598	19.512	45.1074	61.75	82.81
0.7145	1.0569	18.240	48.0090	65.36	82.11
1.0000	1.0410	13.460	60.0000	—	79.77

$R_{obs} = 79.77$

Temp. = 40°.

0.0000	0.9922	6.536	18.0000	22.94	—
0.0446	1.0095	7.993	19.8732	25.54	80.94
0.2111	1.0410	12.210	26.8662	35.19	80.95
0.2322	1.0432	12.550	27.7524	36.51	81.35
0.4251	1.0516	15.170	35.8542	47.92	81.69
0.6452	1.0500	15.330	45.1074	60.41	81.37
0.7145	1.0475	13.810	48.0090	63.65	79.91
1.0000	1.0298	9.076	60.0000	—	76.83

$R_{obs} = 76.83$

Temp. = 50°.

0.0000	0.9880	5.492	18.0000	22.44	—
0.0446	1.0244	6.488	19.8732	25.00	79.82
0.2111	1.0330	9.570	26.8662	34.49	79.53
0.2322	1.0349	9.904	27.7524	35.73	79.67
0.4251	1.0422	11.870	35.8542	47.31	80.96
0.6452	1.0393	11.980	45.1074	59.21	79.43
0.7145	1.0369	11.700	48.0090	63.01	79.23
1.0000	1.0183	7.644	60.0000	—	75.95

$R_{obs} = 75.95$

TABLE II

Ethyl alcohol in water. $R_{\text{calc.}}$ for ethyl alcohol = 73.1

x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x .
Temp. = 30°.					
0.0000	0.9957	8.00	18.00	23.45	—
0.0399	0.9840	10.57	19.11	26.06	88.70
0.0870	0.9723	14.16	20.43	29.26	90.00
0.2048	0.9352	18.71	23.73	36.59	87.50
0.3526	0.8932	17.72	27.87	44.89	84.28
0.6001	0.8457	15.21	33.80	56.16	77.90
0.7404	0.8239	12.25	38.73	64.91	79.40
1.0000	0.7914	9.98	46.00	—	77.5

 $R_{\text{obs}} = 77.5$

Temp. = 40°.					
0.0000	0.9926	6.56	18.00	22.94	—
0.0399	0.9833	8.38	19.11	25.34	83.4
0.0870	0.9690	11.04	20.43	28.45	87.1
0.2048	0.9313	15.17	23.73	35.81	85.78
0.3526	0.8900	13.84	27.87	43.48	80.82
0.6001	0.8405	11.67	33.80	54.68	75.84
0.7404	0.8179	10.42	38.73	63.00	77.87
1.0000	0.7859	8.07	46.00	—	76.76

 $R_{\text{obs}} = 76.76$

Temp. = 50°.					
0.0000	0.9881	5.49	18.00	22.59	—
0.0399	0.9827	6.58	19.11	24.66	74.4
0.0870	0.9674	8.34	20.43	26.88	72.6
0.2048	0.9276	10.01	23.73	34.11	78.01
0.3526	0.8880	10.30	27.87	42.01	77.69
0.6001	0.8335	8.91	33.80	53.31	73.75
0.7404	0.8115	8.16	38.73	61.76	75.51
1.0000	0.7807	7.04	46.00	—	74.54

 $R_{\text{obs}} = 74.54$

TABLE III

Acetone in water. $R_{\text{calc.}}$ for acetone = 84.6.

x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x .
Temp. = 30°.					
0.0000	0.9957	8.004	18.0000	23.45	—
0.1218	0.9505	11.620	22.8720	32.71	99.50
0.1720	0.9216	11.160	24.8700	36.48	99.24
0.3122	0.8919	9.287	30.4880	45.14	92.92
0.3681	0.8819	8.397	32.7240	48.41	91.27
0.6042	0.8311	5.260	42.1600	62.41	87.93
0.7697	0.8066	4.160	48.7880	72.26	86.78
1.0000	0.7811	3.390	58.0000	—	86.46

 $R_{\text{obs}} = 86.46$

TABLE III (contd.)

Temp. = 40°.

x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x .
0.0000	0.9924	6.536	18.0000	22.94	—
0.1218	0.9435	8.966	22.8720	31.88	96.30
0.1720	0.9134	8.596	24.8700	35.63	96.80
0.3122	0.8834	7.082	30.4880	44.06	90.90
0.3681	0.8709	6.751	32.7240	47.65	90.06
0.6042	0.8262	4.571	42.1680	61.70	87.10
0.7697	0.7962	3.656	48.7880	72.02	86.10
1.0000	0.7705	3.089	58.0000	—	86.66

 $R_{obs} = 86.66$

Temp. = 50°.

0.0000	0.9880	5.492	18.0000	22.44	—
0.1218	0.9356	7.087	22.8720	31.23	94.49
0.1730	0.9044	6.847	24.8700	34.97	95.29
0.3122	0.8736	6.027	30.4880	45.67	90.42
0.3681	0.8601	5.547	32.7240	47.12	89.48
0.6042	0.8138	4.055	42.1680	61.12	87.45
0.7697	0.7846	3.421	48.1880	72.49	87.47
1.0000	0.7587	2.871	58.0000	—	87.58

 $R_{obs} = 87.58$

TABLE IV

Methyl alcohol in water. R_{calc} for methyl alcohol = 49.3.

x .	D .	$\eta \times 10^3$.	M_m .	R_m .	R_x .
Temp. = 30°.					
0.0000	0.9957	8.00	18.00	23.45	—
0.1119	0.9703	11.33	19.57	26.44	54.33
0.2752	0.9337	13.04	21.85	31.27	53.21
0.4607	0.8952	12.13	24.42	36.58	52.54
0.6981	0.8476	9.27	27.69	42.60	50.25
0.8322	0.8221	7.46	29.64	45.67	50.25
1.0000	0.7969	5.60	32.00	—	49.72

 $R_{obs} = 49.72$

Temp. = 40°.

0.0000	0.9926	6.56	18.00	22.94	—
0.1119	0.9681	8.58	19.57	26.44	54.34
0.2752	0.9296	9.82	21.85	31.07	53.27
0.4607	0.8910	9.65	24.42	36.58	52.54
0.6981	0.8405	7.82	27.69	42.60	51.10
0.8322	0.8166	6.29	29.64	45.67	50.25
1.0000	0.7912	4.10	32.00	—	48.60

 $R_{obs} = 48.6$

Temp. = 50°.

0.0000	0.9881	5.49	18.00	22.59	—
0.1119	0.9681	7.44	19.57	25.98	53.01
0.2752	0.9276	7.88	21.85	30.49	51.31
0.4607	0.8880	7.70	24.42	35.65	50.93
0.6981	0.8364	6.27	27.69	41.65	49.79
0.8322	0.8117	5.39	29.64	45.07	49.48
1.0000	0.7880	3.99	32.00	—	47.97

 $R_{obs} = 47.97$

The results with acetic acid in water show that the value of R_{obs} for various concentrations of acetic acid are in good agreement with one another, although this value differs by four units from the R_{obs} for the pure acid. Considering the fact that R_x is to be determined by the expression

$$R_m = R (1-x) - xR_x$$

which magnifies the small error in R_m , when R_x is calculated, the agreement between R_{obs} and R_x may be regarded as fair. In other words, the mixture law seems to be applicable for the rheochor of acetic acid in water.

In case of acetone, ethyl alcohol and methyl alcohol as solutes in water, very high values are obtained for R_x at lower concentrations than the values for pure liquids. The values fall and approach the R_{obs} for pure liquid as the concentration is increased, but there seems to be no linear relation between R_x and the concentration of the solute. In all cases R_{obs} and R_x decrease with increase of temperature and approach R_{calc} since the calculated values correspond to the boiling point of the liquid solute.

CHEMISTRY DEPARTMENT,
HOLKAR COLLEGE,
INDORE

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THE STUDY OF IMPERFECT COMPLEXES. PART I. CALORIMETRIC STUDY OF COMPLEXES BY JOB'S METHOD OF CONTINUED VARIATION

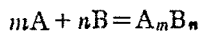
By SUSHIL KUMAR SIDDHANTA

Job's method of continued variation has been applied by several workers for the determination of the composition and the dissociation constant of complexes of low stability from a study of properties like extinction coefficient, conductivity, refractivity, etc. In the present work, it has been shown that the molar heat content can be utilised as a property, the variation of which may be employed for the same purpose.

Thermometric titrations were first introduced by Dutoit (*J. chim. phys.*, 1921, 19, 324) to determine the composition of new compound or compounds formed in solution by mixing solutions of two compounds. In this method the temperature change observed on adding gradually the solution of one compound to a definite volume of that of another was plotted against the volume of the first solution added, and the compositions of the new compounds formed in solution were taken to be indicated by the inflexion points. Such a simple method, in the opinion of the present author, is apt to give in many cases inaccurate information as to the composition of the new substance or substances formed. A detailed discussion on this point will be given in Part III of this series.

Titration, using certain molecular properties, such as conductivity, as a guide for the determination of reacting proportions are also in use for a long time. Such a method also, it may be remarked, gives a sharp inflexion point only when a perfect complex is formed and is apt to give inaccurate information about imperfect complexes having large dissociation constant (vide Part III of the series).

Job's method of continued variation for the study of imperfect complexes (Job, *Compt. rend.*, 1925, 180, 928; *Ann. Chim.*, 1928, x, 9, 113) using an additive molecular property as guide is, however, more reliable in cases where only one complex is formed by mixing two solutions. The method gives not only the composition of the complex formed, but its approximate dissociation constant in addition. In the following reaction between two molecules A and B,



if $(1-x)$ c.c. of a solution of A of molar concentration c per c.c. be added to x c.c. of a solution of B of molar concentration c' per c.c. ($c' = pc$), and if C_1 , C_2 , C_3 be the respective molar concentrations per c.c. of A, B, and A_mB_n after the equilibrium has been attained, the following equations apply for any such mixture.

$$C_1^m \cdot C_2^n = K \cdot C_3 \quad \dots \quad (A)$$

where K is the dissociation constant of the complex.

$$C_1 + mC_3 = c(1-x) \quad \dots \quad (B)$$

$$C_2 + nC_3 = pcx \quad \dots \quad (C)$$

Starting from relations (A), (B), (C) Job showed that equation (1) is true only for that value of x for which C_3 is maximum.

$$\frac{c^{m+n-1} \cdot p^{n-1} \{ (pm+n)x - n \}^{m+n}}{m^{n-1} \cdot n^{m-1}} = K \cdot \{ n - (m+n)x \} (p-1)^{m+n-1} \quad \therefore (1)$$

when $p=1$ (i.e., for equimolecular parent solutions), the right hand side of equation (1) is zero and therefore

$$m/n = 1 - x/x \quad \dots (2)$$

as c, p, m and n are finite constants.

Hence, from a knowledge of the value of x where C_3 is maximum, the formula of the complex can be determined from the ratio m/n using equation (2), taking simplest integral values of m and n provided that the two primary solutions used are of equimolecular concentration. After determining thus the values of m and n , the value of K can be determined by equation (1) using the value of x for maximum C_3 in the case of two-primary solutions which are not equimolecular (i.e., where $p \neq 1$).

The problem then obviously reduces to the determination of the value of x for which the concentration C_3 of the complex A_mB_n is maximum, using both equimolecular and non-equimolecular primary solutions of A and B. This offers no special difficulty when A_mB_n has a property not possessed by A and B; then the value of x , where this property is maximum, gives the maximum value of the concentration C_3 of the complex A_mB_n . Usually, however, such a property is difficult to be found. In such cases, Job proposed to study as a function of x any molecular property which obeys the mixture law in the following way:

$$P_{\text{mixture}} = \alpha P_A + \beta P_B + \gamma P_C + \dots$$

where $\alpha, \beta, \gamma, \dots$ are the number of moles of A, B, C, ... present in the solution and P_A, P_B, P_C, \dots are the respective molar values of the property P for A, B, C, ...

Job has mathematically showed that the difference, Y , of the observed value of the property P for any mixture of x c.c. of a solution of B and $(1-x)$ c.c. of a solution of A from that calculated for the mixture by the additivity rule with the assumption that no reaction takes place when plotted against the different corresponding values of x , gives a curve, the maximum (or minimum) point of which represents the value of x where C_3 is maximum.

Job (*loc. cit.*) chose molar extinction coefficient as the property to be studied and he determined it spectrophotometrically for various solutions of pure A and B and their mixtures in order to find out the value of Y for different values of x . The same property has been used by Vorsburgh and co-workers (*J. Amer. Chem. Soc.*, 1941, **63**, 437; 1942, **64**, 1630) to determine the composition of a number of imperfect complexes; these workers also modified Job's method to the study of composition in a few cases, where more than one complexes are formed in solution.

Spacu and Popper (*Bull. Soc. Stiinta, Cluj*, 1934, **7**, 400; 1934, **8**, 5) have used molar refractivity as an indicative property to be studied by Job's method. Molar conductivity has also been used by a number of workers as a guide for the study of complex compounds in solution by Job's method (Dutt, paper communicated to Indian

Chemical Society; Purkayastha and Sen-Sarma, *J. Indian. Chem. Soc.*, 1946, **23**, 31; Purkayastha, *ibid*, 1947, **24**, 257; 1948, **25**, 81; Biswas, *ibid.*, 1947, **24**, 345). Biswas (*loc. cit.*) has also studied as a function of the composition of the mixture, the difference of the observed H^+ ion concentration of the mixture from that calculated by additivity rule with the assumption of no reaction taking place in order to determine the composition of the complex formed in solution between molybdic and tartaric acids.

In the present paper, it is proposed that molar heat content is a suitable property to be studied in Job's method of continued variation, so that the deviation Y from the additivity rule is given by the heat of reaction ($-\Delta H$). But since the reaction is to be studied in solution, the heats of solution of the reactants and of the resultant should be considered.

Thus, the heat content of $(1-x)$ c.c. of a solution of A at concentration c

$$= (1-x) \left\{ c \cdot H_A + c q_A + \frac{1}{18} H_{H_2O} \right\}$$

and the heat content of x c.c. of a solution of B at concentration pc

$$= x \left\{ pc \cdot H_B + pc q_B + \frac{1}{18} H_{H_2O} \right\}$$

where H_A , H_B and H_{H_2O} are the respective molar heat contents of A, B and H_2O and $c q_A$ and $pc q_B$ are the respective heats of solution of c mols. of A and pc mols. of B, both in 1 c.c. of water, supposing however, that no change of volume takes place on dissolution of solutes and that 1 c.c. of any solution contains $\frac{1}{18}$ mols. of H_2O .

The sum of the heat contents of the two parent solutions before mixing is therefore given by

$$H_{\text{reactants}} = (1-x) \left\{ c \cdot H_A + c q_A \right\} + x \left\{ pc \cdot H_B + pc q_B \right\} + \frac{1}{18} H_{H_2O}.$$

By mixing the two parent solutions, we get 1 c.c. of the mixture which after attainment of equilibrium contains C_1 mols. of A, C_2 mols. of B and C_3 mols. of A_mB_n . Proceeding as above with the use of analogous notation, and supposing that there is no volume change on mixing the two solutions and that 1 c.c. of any solution contains $\frac{1}{18}$ mols. of H_2O , we can calculate $H_{\text{resultant}}$ of 1 c.c. of this mixture.

$$H_{\text{resultant}} = C_1 \cdot H_A + c_1 q_A + C_2 \cdot H_B + c_2 q_B + C_3 \cdot H_{A_mB_n} + c_3 q_{A_mB_n} + \frac{1}{18} H_{H_2O}.$$

The heat of reaction is therefore given by

$$\begin{aligned} (-\Delta H) &= H_{\text{reactants}} - H_{\text{resultant}} \\ &= (1-x) \{ c \cdot H_A + c q_A \} + x \{ pc \cdot H_B + pc q_B \} - \{ C_1 \cdot H_A + c_1 q_A + C_2 H_B + c_2 q_B \\ &\quad + C_3 \cdot H_{A_mB_n} + c_3 q_{A_mB_n} \} \quad \dots (3) \end{aligned}$$

Now, by the law of partial molal quantities,

${}_o q_A$ = heat of solution of c mols. of A in 1 c.c. of water

$$= c \cdot {}_o \bar{q}_A + \frac{1}{18} c \bar{q}_{(H_2O)A} \quad \dots (4)$$

where \bar{q}_A is the differential heat of solution A at concentration c , i.e., heat change due to dissolution of 1 mol. of A in a large volume of a solution of A at concentration c and $\bar{q}_{(H_2O)A}$ is the differential heat of dilution for a solution of A at concentration c i.e., heat change due to the addition of 1 mol. of H_2O in a large volume of a solution of A at concentration c .

If the solutions used be moderately dilute so that the heat change due to addition of further amount of water may be neglected, we may neglect the quantity $c \bar{q}_{(H_2O)A}$ in equation (4). Also ${}_o \bar{q}_A$ is practically equal to ${}_o q_A$, the heat of solution of 1 mol. of A in a large volume of pure water (instead of in a solution of A at concentration c).

Hence equation (4) can be written as

$${}_c q_A = c \cdot {}_o \bar{q}_A.$$

Proceeding similarly and using analogous notations, we may have ... (4a)

$${}_p c q_B = p c \cdot {}_o \bar{q}_B \quad \dots (4b)$$

$${}_c q_A = C_1 \cdot {}_o \bar{q}_A \quad \dots (4c)$$

$${}_c q_B = C_2 \cdot {}_o \bar{q}_B \quad \dots (4d)$$

$${}_c q_{AmBn} = C_3 \cdot {}_o \bar{q}_{AmBn} \quad \dots (4e)$$

Putting (4a, b, c, d, e) in (3) we have

$$(-\Delta H) = (1-x) c \left\{ H_A + {}_o \bar{q}_A \right\} + x p c \left\{ H_B + {}_o \bar{q}_B \right\} - \left[C_1 \left\{ H_A + {}_o q_A \right\} + C_2 \left\{ H_B + {}_o \bar{q}_B \right\} + C_3 \left\{ H_{AmBn} + {}_o \bar{q}_{AmBn} \right\} \right] \quad \dots (3a)$$

Writing C_1 and C_2 in equation (3a) in terms of C_3 using equations (B) and (C), we have

$$(-\Delta H) = m C_3 \left\{ H_A + {}_o \bar{q}_A \right\} + n C_3 \left\{ H_B + {}_o \bar{q}_B \right\} - C_3 \left\{ H_{AmBn} + {}_o \bar{q}_{AmBn} \right\} \quad \dots (3b)$$

Since $H_A, H_B, H_{AmBn}, {}_o \bar{q}_A, {}_o \bar{q}_B, {}_o \bar{q}_{AmBn}$ are constants we have by differentiating (3b) with respect to x ,

$$\frac{d(-\Delta H)}{dx} = \frac{dC_3}{dx} \left[m \left\{ H_A + {}_o \bar{q}_A \right\} + n \left\{ H_B + {}_o \bar{q}_B \right\} - \left\{ H_{AmBn} + {}_o \bar{q}_{AmBn} \right\} \right] \quad \dots (5)$$

From equation (5) we have

$$\frac{d(-\Delta H)}{dx} = 0, \text{ when } \frac{dC_3}{dx} = 0$$

i. e., $(-\Delta H)$ must be at a maximum or a minimum for that value of x for which C_s is maximum.

The heat of reaction $(-\Delta H)$ due to mixing x c. c. of a solution of ammonia with $(100-x)$ c.c. of a solution of copper sulphate at equimolecular and non-equimolecular concentrations has been studied by Siddhanta and Guha (details will appear in Part III of this series). It has been shown that for equimolecular solutions the value of x , where $(-\Delta H)$ is maximum, lies at 80 c.c. So that $m/n=1:4$ by equation (2) i. e., complex ion formed is $[\text{Cu}(\text{NH}_3)_4]^{++}$; also using non-equimolecular solutions the values of x , where $(-\Delta H)$ is maximum, have been utilised to calculate K , the dissociation constant of this complex, by applying equation (1). The value of K obtained in this way accords fairly well with that obtained by Job from the study of molar extinction coefficients by the method of continued variation. The special advantage of this process discussed above is that it directly gives the difference Y (i. e., $-\Delta H$) from the additivity rule for any mixture by one reading only. But if any other property be chosen to be studied, three readings of the property will be necessary to find out Y for any mixture—two readings for the two parent solutions and the third for the mixture. The process, introduced here, is therefore more direct and takes much shorter time in comparison with any other prevalent process of study by Job's method of continued variation. Another remarkable feature of the process is that it gives the value of both K and $(-\Delta H)$ and hence the approximate value of the free energy change $(-\Delta F)$ and the entropy change $(-\Delta S)$ of the complex formation can be calculated by the well known relations

$$(-\Delta F) = RT \ln K$$

$$(-\Delta H) = (-\Delta F) + T(-\Delta S).$$

There is, however, one serious limitation to the process that should be mentioned here. If the heat of dilution of the parent solutions used be not negligible in comparison with the heat of formation of the complex, the process will fail to yield good results. In the author's estimate, the process is workable if the heats of dilution of the parent solutions used do not exceed 10% of the value of the heat of formation of the complex.

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CHEMICAL LABORATORY,
PRESIDENCY COLLEGE,
CALCUTTA.

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THE STUDY OF IMPERFECT COMPLEXES. PART II. A MODIFICATION OF JOB'S METHOD OF CONTINUED VARIATION: STUDY OF IMPERFECT COMPLEXES BY CALORIMETRY

BY SUSIL KUMAR SIDDHANTA

The equation, forming the basis of Job's method of continued variation for the determination of the composition and stability of imperfect complexes, has been modified so that the experimental procedure may be simplified and rapidly executed.

Job's method of continued variation (*Compt. rend.*, 1925, 130, 938; *Ann. chim.* 1928, x, 9, 113) has been discussed in Part I of this paper (this issue, p. 579). In that method the formula of the complex and its dissociation constant K could be found by studying a suitable property of the mixture of x c.c. of a solution of B with $(1-x)$ c.c. of a solution of A, the reaction being



From the experimental point of view, the method is, however, a laborious one as it involves the mixing of a large number of independent x and $(1-x)$ volumes of the two parent solutions for studying the property of the mixture for any one particular set of concentrations of the parent solutions.

In the present communication it has been shown that Job's method, with a little modification, is applicable also to the ordinary continuous titration experiments in which a constant amount ' a ' c.c. of a solution of A is titrated with a gradually increasing amount of x c.c. of the solution of B.

Let c and pc be the molar concentrations per c.c. of the solutions of A and B respectively; let at any particular instant x c.c. of the solution of B be added to a constant volume ' a ' c.c. of the solution of A and let C_1 , C_2 , C_3 be the molar concentrations of A, B and A_mB_n in the resulting mixture after attainment of equilibrium. For any volume of x , the following three relations apply

$$C_1^m \cdot C_2^n = K \cdot C_3 \quad \dots (1)$$

where K is the dissociation constant of the complex

$$(a+x)C_1 + (a+x)mC_3 = ac$$

$$\text{or} \quad C_1 = \frac{ac}{a+x} - mC_3 \quad \dots (2)$$

$$\text{and} \quad (a+x)C_2 + (a+x)nC_3 = pcx$$

$$\text{or} \quad C_2 = \frac{pcx}{a+x} - nC_3 \quad \dots (3)$$

Putting (2) and (3) in (1) we have,

$$\left\{ \frac{ac}{a+x} - mC_3 \right\}^m \cdot \left\{ \frac{pcx}{a+x} - nC_3 \right\}^n = KC_3 \quad \dots (4)$$

Since C_3 is a function of the only variable x , C_3 will be at a maximum when $\frac{dC_3}{dx} = 0$.

Differentiating (4) with respect to x regarding p, c, a, m, n and K as constants, and putting $\frac{dC_3}{dx} = 0$ in the resulting equation, we obtain equation (5) which is true only for that value of x , for which C_3 is maximum.

$$C_3 = \frac{pc(na - mx)}{(a+x)(p-1)mn} \quad \dots (5)$$

Putting (2), (3) and (5) in (1) we get equation (6) which also is true only for that value of x for which C_3 is maximum

$$K = \frac{c^{m+n-1} \cdot p^{n-1} (pmx - an)^{m+n}}{n^{m-1} m^{n-1} (a+x)^{m+n-1} \cdot (p-1)^{m+n-1} (na - mx)} \quad \dots (6)^*$$

Equation (6) may be written as

$$c^{m+n-1} \cdot p^{n-1} \cdot (pmx - an)^{m+n} = K \cdot n^{m-1} \cdot m^{n-1} \cdot (a+x)^{m+n-1} \cdot (p-1)^{m+n-1} \cdot (na - mx) \quad (6a)$$

when $p=1$ (i. e., for equimolecular primary solutions), right hand side of equation (6a) is zero and since c, p, m and n are finite constants, we have

$$pmx - an = 0$$

$$\text{or } m/n = a/x \quad \dots (7)$$

$$\text{since } p=1.$$

Thus, using equimolecular primary solutions of A and B, we can find out the ratio m/n i. e., the formula A_mB_n of the complex using simplest integral values of m and n , provided we can find out the value of x where C_3 is maximum with equimolecular primary solutions. After determining thus the values of m and n , the dissociation constant K of the complex can be determined by equation (6) or (6b) using two non-equimolecular primary solutions provided we can determine the value of x where C_3 is maximum with these two solutions.

To determine the value of x where C_3 is maximum, we can proceed in a way analogous to that in Job's method. As in Job's method an additive molecular property P , such as molar extinction coefficient as suggested by Job or molar refractivity as used by Spăcu and Popper or molecular conductivity as employed by various workers (for reference, see Part I of this paper, this issue, p 579) should be studied for the two pure

* Where $p < 1$, the value of K should be calculated by (6b) instead of (6).

$$K = \frac{c^{m+n-1} \cdot p^{n-1} \cdot (an - pmx)^{m+n}}{n^{m-1} \cdot m^{n-1} \cdot (a+x)^{m+n-1} \cdot (1-p)^{m+n-1} \cdot (mx - na)} \quad \dots (6b)$$

which can be arrived at by using $C_3 = \frac{pc(mx - na)}{(a-x)(1-p)mn}$ which is another form of equation (5)

primary solutions and for their various mixtures. Since x c.c. of a solution of B at concentration pc per c.c. is added to a constant amount ' a ' c.c. of a solution of A at concentration c per c.c. at any instant, and since C_1, C_2, C_3 are the respective concentrations per c.c. of A, B, and A_mB_n in the resulting solution after attainment of equilibrium, the observed value of the property P for such a mixture is given by

$$P_{\text{obs.}} = (a+x) \{C_1 P_A + C_2 P_B + C_3 P_{A_mB_n}\} \quad \dots (8)$$

where P_A, P_B and $P_{A_mB_n}$ are the respective molar values of the property P for A, B and A_mB_n .

Had no complex been formed, the property P for the above mixture would have been given by

$$P_{A, B} = ac. P_A + pcx. P_B. \quad \dots (9)$$

Therefore the difference Y from the additivity rule is given by

$$Y = P_{A, B} - P_{\text{obs.}} = ac. P_A + pcx. P_B - (a+x) \{C_1 P_A + C_2 P_B + C_3 P_{A_mB_n}\} \quad \dots (10)$$

writing in equation (10), C_1 and C_2 in terms of C_3 using equations (2) and (3) we have

$$Y = (a+x) C_3 \{m.P_A + n.P_B - P_{A_mB_n}\} \quad \dots (10a)$$

$$\text{or } C_3 \{m.P_A + n.P_B - P_{A_mB_n}\} = Y/a+x = f \text{ (say)} \quad \dots (10b)$$

where f is a new function of x .

Differentiating (10b) with respect to x , we have

$$df/dx = \{m.P_A + n.P_B - P_{A_mB_n}\} \frac{dC_3}{dx} \quad \dots (11)$$

By (11), it is easily seen that when $dC_3/dx=0$, df/dx is also zero. Thus when the concentration C_3 of the complex is at a maximum, the value of the function f (i. e., $Y/a+x$) must be at a maximum or a minimum according as $mP_A + n.P_B$ is greater than or less than $P_{A_mB_n}$.

Hence, by studying $Y/a+x$ as a function of x (i. e., plotting the value of $Y/a+x$ against the corresponding values of x), we can get the value of x where $Y/a+x$ is maximum or minimum, and this value of x represents the point where C_3 is maximum.

In Part I of this paper (*loc. cit.*) the molar heat content has been shown to be a property suitable for study by Job's method of continued variation. It can easily be shown that molar heat content is also a property, the variation of which can be studied in this present modified method of Job for determining the composition and the stability of a complex.

The sum of heat contents of ' a ' c.c. of a solution of A at concentration c per c.c. and of x c.c. of a solution of B at concentration pc per c.c. before mixing, is given by

$$H_{\text{reactants}} = a \left\{ c.H_A + cq_A + \frac{1}{18}H_{H_2O} \right\} + x \left\{ pc. H_B + pq_B + \frac{1}{18}H_{H_2O} \right\}$$

and the heat content of the mixture of the two aforesaid solutions after the attainment

of equilibrium is given by

$$H_{\text{resultant}} = (a+x) \{ C_1 H_A + c_1 q_A + C_2 H_B + c_2 q_B + C_3 H_{A_m B_n} + c_3 q_{A_m B_n} + \frac{1}{18} H_{H_2O} \}$$

where H_A , H_B , $H_{A_m B_n}$ and H_{H_2O} are the respective molar heat contents of A, B, $A_m B_n$ and H_2O , $c_1 q_A$ is the heat of solution of c mols. of A in 1 c.c. water and $p c q_B$, $c_2 q_A$, $c_3 q_B$ and $c_3 q_{A_m B_n}$ have analogous meanings, assuming however that no change of volume of the liquid takes place on dissolution of solutes and that 1 c.c. of any solution contains 1/18 mols. of H_2O .

Hence, assuming that no change of volume takes place on mixing the solutions, the heat of reaction is given by

$$\begin{aligned} (-\Delta H) &= H_{\text{reactants}} - H_{\text{resultant}} \\ &= a \{ c H_A + c_1 q_A \} + x \{ p c H_B + p c q_B \} - (a+x) \{ C_1 H_A + c_1 q_A + C_2 H_B + c_2 q_B + \\ &\quad C_3 H_{A_m B_n} + c_3 q_{A_m B_n} \} \quad \dots (12) \end{aligned}$$

Proceeding as in Part I of this paper, we can prove for dilute solutions that

$$c_1 q_A = c \cdot \bar{o} q_A \quad \dots (13a)$$

$$p c q_B = p c \cdot \bar{o} q_B \quad \dots (13b)$$

$$c_2 q_A = C_1 \cdot \bar{o} q_A \quad \dots (13c)$$

$$c_3 q_B = C_2 \cdot \bar{o} q_B \quad \dots (13d)$$

$$c_3 q_{A_m B_n} = C_3 \cdot \bar{o} q_{A_m B_n} \quad \dots (13e)$$

where $\bar{o} q_A$ is the molar heat of solution of A in a large volume of water, and $\bar{o} q_B$ and $\bar{o} q_{A_m B_n}$ carry analogous significance; the three quantities $\bar{o} q_A$, $\bar{o} q_B$ and $\bar{o} q_{A_m B_n}$ can be regarded as constants.

Putting equations (13a, b, c, d, e) in equation (12) we have

$$\begin{aligned} (-\Delta H) &= a c \left\{ H_A + \bar{o} q_A \right\} + p c x \left\{ H_B + \bar{o} q_B \right\} - (a+x) \left[C_1 \left\{ H_A + \bar{o} q_A \right\} + C_2 \left\{ H_B + \bar{o} q_B \right\} + \right. \\ &\quad \left. C_3 \left\{ H_{A_m B_n} + \bar{o} q_{A_m B_n} \right\} \right] \quad \dots (12a) \end{aligned}$$

The form of equation (12a) is similar to that of equation (10), and proceeding in an analogous manner as in that case, we can prove that the value of the function $(-\Delta H)/a+x$ must be maximum or minimum for that value of x for which C_3 is maximum.

The heat of reaction $\delta(-\Delta H)$ due to the successive equal additions, Δx c.c. each time, of a solution of copper sulphate at concentration $p c$ per c.c. to a constant volume 'a' c.c. of a solution of ammonia at concentration c has been determined by Siddhanta and Guha (vide Part III of this series, under publication) and the values of $(-\Delta H)/a+x$ have been plotted against the corresponding values of x [$(-\Delta H) = \Sigma \delta(-\Delta H)$ and $x = \Sigma \Delta x$].

It has been shown that for equimolecular primary solutions, $(-\Delta H)/a+x$ is maximum where $x=\frac{1}{4}a$, whence $m/n=4:1$ i. e., the composition of the complex is $[\text{Cu}(\text{NH}_3)_4]^{++}$. Using non-equimolecular primary solutions, the values of x where $(-\Delta H)/a+x$ is maximum have been utilised to calculate dissociation constant K of the complex by equation (6b), p being chosen less than one. The value of K thus determined accords fairly well with that determined by Job (*loc. cit.*) and that by Siddhanta and Guha by the calorimetric application of Job's method, described in detail in Part I (*loc. cit.*) and Part III of this series (to be published).

This modification of Job's method as applied to calorimetry carries all the advantages of his method of continued variation, the study being made in an analogous manner namely by observing the heats of reaction. The modification has an additional advantage of being continuous and very rapid from the experimental point of view. It has, however, the limitation discussed in Part I of this paper that the solutions used should have negligible heats of dilution.

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CHEMICAL LABORATORY,
PRESIDENCY COLLEGE,
CALCUTTA.

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COMPLEX COMPOUNDS OF BIGUANIDE WITH TERVALENT METALS.
PART XIII. AMPHOLYTIC INNER-METALLIC COBALTIC COMPLEXES
WITH NAPHTHYLBIGUANIDE *o*-SULPHONIC ACID AND PHENYL-
BIGUANIDE *p*-SULPHONIC ACID AND THEIR SALTS

BY PRIYADARANJAN RÂY AND RABINDRA KUMAR DUTT

The ampholytic complex of tervalent cobalt with naphthylbiguanide *o*-sulphonic acid has been prepared, and its alkali salts, as well as as those of the corresponding phenylbiguanide *p*-sulphonic acid complex, have been described.

In a previous paper (this issue, p. 563) the preparation and properties of the alkali salts of the ampholytic complexes of bivalent copper and nickel with naphthyl and phenylbiguanide sulphonic acids have been described. The present paper deals with the study of the alkali salts of the corresponding tervalent cobalt complexes.

The octahedral ampholytic cobaltic complexes with α -naphthylbiguanide *o*-sulphonic acid or phenylbiguanide *p*-sulphonic acid might exist in two geometrical forms.

This arises from the difference in the relative positions of the aromatic groups to each other in the molecule. But only one form of the complex in each case has actually been isolated.

EXPERIMENTAL

1. *Cobaltic Naphthylbiguanide o-Sulphonic Acid*.—Naphthylbiguanide *o*-sulphonic acid (4.5 g.) was dissolved in an excess of warm concentrated ammonia; to this a solution of cobalt chloride (1g.) was added, followed by a solution of H_2O_2 . The precipitate, first formed, changed from light rose to brown. The mixture was heated and filtered. To the filtrate a vigorous current of air was passed for about 24 hours. The mixture was then evaporated on the water-bath till there was no smell of ammonia. On cooling, a brown precipitate separated. This was washed first with water, then with alcohol, and finally dried in air. {Found: N, 19.36; Co, 5.42. $Co(HO_3S.Nap.Big)_3.6H_2O$ requires N, 19.36; Co, 5.45 per cent}. $NapBigH$ =a molecule of naphthylbiguanide.

The substance forms brown crystals, slightly soluble in water and dilute ammonia, but readily in caustic alkali,

2. *Potassium Cobaltic Naphthylbiguanide o-Sulphonate*.—Cobaltic naphthylbiguanide *o*-sulphonic acid (4 g.) was dissolved in moderately concentrated solution of KOH. The solution was concentrated on the water-bath. On the addition of alcohol to the cold solution a brown precipitate separated out. This was purified by dissolving it in the least quantity of water and then reprecipitating with absolute alcohol. It was washed first with 90% alcohol, then with absolute alcohol, and finally dried in air. {Found: N, 17.91; Co, 4.98; K, 9.95. $K_3[Co(SO_3NapBig)_3].5H_2O$ requires N, 17.82; Co, 5.0; K, 9.93 per cent}.

The substance forms brown crystals, highly soluble in water. It reacts alkaline to litmus.

3. *Sodium cobaltic naphthylbiguanide o-sulphonate* was prepared like the potassium salt by substituting NaOH for KOH. It resembles the latter salt in properties. {Found : N, 19.57 ; Co, 5.48 ; Na, 6.44. $\text{Na}_3[\text{Co}(\text{SO}_3\text{NapBig})_3] \cdot 2\text{H}_2\text{O}$ requires N, 19.55 ; Co, 5.49 ; Na, 6.43 per cent}.

4. *Potassium cobaltic phenylbiguanide p-sulphonate* was prepared like the potassium salt of the corresponding naphthylbiguanide complex. It forms highly soluble brown powder. {Found : N, 20.96 ; Co, 5.90 ; K, 11.68. $\text{K}_3[\text{Co}(\text{O}_3\text{S. PhBig})_3] \cdot 3\text{H}_2\text{O}$ requires N, 21.06 ; Co, 5.91 ; K, 11.72 per cent}.

5. *Sodium cobaltic phenylbiguanide p-sulphonate* was prepared in the same way as the sodium salt of the corresponding naphthylbiguanide complex, and it resembles the latter in properties. {Found : N, 20.61 ; Co, 5.76 ; Na, 6.71. $\text{Na}_3[\text{Co}(\text{O}_3\text{S. PhBig})_3] \cdot 7\text{H}_2\text{O}$ requires N, 30.61 ; Co, 5.79 ; Na, 6.77 per cent}. PhBigH = a molecule of phenylbiguanide.

INORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE OF SCIENCES,
CALCUTTA.

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ON AN APPARENTLY TRIBASIC ACID CHARACTER OF HYDROGEN MICA

BY R. P. MITTER AND K. S. RAJAGOPALAN

The lattice-structure of muscovite is well known mainly through the work of Jackson and West (*Z. Kristallog.*, 1931, 79, 2). On comminution, the weak K-O bonds of the lattice readily break giving platelets with K ions exposed on *a-b* planes. Finely ground muscovite was leached with dilute HCl to obtain hydrogen- or, acid-mica by the replacement of the exposed potassiums by hydrogen ions. Aqueous suspensions of this hydrogen mica were found to behave as weak tribasic acids judged from their potentiometric titration curves with NaOH and KOH. The first inflexion in the titration curve, which is often very weak, occurs near about p_H 7.0. The other two inflexions are much more prominent and they are located at about p_H 9.0 and 10.5. The presence of H-ions in three distinct affinity levels on the surface is indicated. The significance of these levels is brought out on a comparison of the amounts of acid neutralised at the three inflexion points. A particular specimen gave the acidity values (A.V) 3.2, 14.0 and 42.0 in m. e., per 100 g. of dry matter calculated respectively at the first, second and third inflexions. K ions to the extent of 14.0 m.e. were also displaced from 100 g. of the ground muscovite in preparing the hydrogen mica.

The observed agreement between the quantity of displaced K found in the HCl extract of the original ground material and the A.V. at the second inflexion of the resulting hydrogen mica shows that this inflexion marks the completion of the neutralisation of H-ions acquired by the surface of the platelets in exchange for their exposed potassium ions. Such H-ions are, of course, bonded to the surface by the negative charges arising from the isomorphous replacement of every fourth Si ion in the tetrahedral layer of the lattice by an Al ion.

The A. V.'s calculated at the third and second inflexions of the titration curve are as 3:1. This is consistent with the idealised formula, $H^*(Al_2)(AlSi_3)O_{10}(OH)_2$, of hydrogen mica and with the assumption that for each H ion (marked with an asterisk in the formula) of the above category, the two OH groups, which are structurally identical, react with the base through hexagonal rings of oxygens at the third, or, final inflexion. The portion of the titration curve between the second and third inflexions thus corresponds to the neutralisation of H ions dissociated from these OH groups.

The significance of the first (weak) inflexion in the titration curve is not quite apparent on the basis of the chemical composition of muscovite and its atomic structure as deduced from X-ray analysis (Jackson *et al.*, *loc. cit.*). This inflexion appears to differentiate between the H ions acquired by the surface in exchange for the exposed potassiums and it seems to allocate them between two sub-levels of affinity on the surface. H ions at flake edges and corners would, of course, have bonding energies different from those on the cleavage planes. Other factors also require to be considered. They will be fully discussed elsewhere.

The observed weak acid character of hydrogen mica fails to confirm Pauling's prediction ("Nature of Chemical Bonds", Cornell University Press, Ithaca, 1939, p. 376) that it should behave as a very strong acid judged from his electrostatic valence rules as applied in this case to linked Si-O and Al-O tetrahedra. Apparently, factors not coming within the purview of these rules and not immediately deducible from them have to be considered. This will be done in a separate communication.

CHEMISTRY DEPARTMENT,
DELHI UNIVERSITY.

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REVIEWS

Organic Analytical Reagents. Vol. I and Vol. II. By F. J. Welcher Published by Van Nostrand, New York, 1947, pp. 448 + xv. Price 40/-sh.

These are the first two of a series of volumes on what has been aimed by the author to be a complete assembly of all organic compounds used in the analysis of inorganic substances. The uses cover the widest possible field as it is evident from the inclusion of ether as a reagent in the detection of boric acid by volatilization or of acetyl chloride in the determination of water in organic media. In most cases selected methods have been given for preparation of the compounds listed.

A distinctive feature in the plan of the book has been to classify the reagents, in the manner of the organic chemist, into sections of chemically similar types of compounds, such as, the hydrocarbons, quinoline derivatives, amines etc. This is likely to stimulate further work in the field, although, as the author has pointed out, this has led to wide scattering of well known oxidising and reducing agents, which are very much allied from the analytical point of view, throughout the body of the treatise. The other feature, viz., collection in one place of all information of a given compound on analytical uses, preparations, references, etc. has some obvious disadvantages which have been largely eliminated by the inclusion of two useful indexes at the end, viz., of the names of the reagents and applications of the reagents classified separately in each volume.

In the first fifty pages of Vol. I, an elementary discussion on the broad principles of bond and ring formation and on the effect of structure and other factors on solubility has been given. Following that, Vol. I contains sections on hydrocarbons and their substitution products, alcohols, phenols and phenolic compounds, 8-oxyquinoline and its derivatives, ethers, aldehydes and ketones. Vol. II contains sections on acids, acid halides, acid anhydrides, esters and quarternary ammonium compounds, besides a big section on amines covering nearly half of the volume.

A meticulous collection of references has been a welcome feature of the book. The literature has been collected, so far as was practicable under conditions resulting from the war, up to the end of 1945.

J. G.

Statistical Methods in Research and Production (with special reference to the Chemical Industry). Edited by Owen L. Davies. Published by Oliver and Boyd, London, pp. 292 + xii. Price 28/- sh.

Statistical analysis is indispensable whenever one has to disentangle the effects of a simple cause system, in which one is interested, from data affected with a multiplicity of causes. And this situation does not obtain anywhere else so strikingly as in an industrial production process. The production manager or technician of every industry knows only too well how difficult it is to maintain the quality of a product at a specified level, and that is so in spite of all possible care and supervision. The new technique

of statistical Quality Control is a powerful tool in his hands to detect and eliminate major causes of variation in the quality of a product, and to reduce this inherent variation to an economic minimum. In this way is attained a state of uniformity in the production process which makes possible the predictions about the future quality of the product.

The book under review gives an elementary exposition of the basic statistical methods which are no doubt available in the existing literature of statistics, but its main object is to "bring together under one cover those statistical methods which are most likely to be of use in the Chemical Industry". To fulfil this objective it begins with a discussion of frequency distribution, average and dispersion, devotes one chapter each to tests of significance, analysis of variance, regression and correlation and contingency tables; and in the last three chapters (viz. 8, 9, 10) it explains the different sampling procedures applicable to chemical industry, the use of control charts and the problem of prediction and specification. It contains a large number of illustrations from various types of problems arising in chemical industry which, besides demonstrating the calculating procedures, serve to impress upon the ordinary reader the importance of statistical methods in a chemical production process.

It, however, appears from a study of the various chapters that the objective set up in the beginning was followed in a very limited sense. In fact, it describes fully only those methods which have been actually applied by the authors, while various other methods which are being applied increasingly elsewhere do not get adequate treatment and sometimes they have not been touched upon at all. Most regrettable is the omission of the group of non-parametric tests which are very much in use in this field in these days. One would also like to see the subject of prediction and specification more fully developed, as also an elaboration of the sampling procedures discussed in chapter 8. If the book is really "to be of considerable use to people engaged in research and process work", it should give a fuller exposition of the statistical principles and not merely the mechanical procedures for applying it to a number of enumerated cases.

H. K. N.

Major Instruments of Science and their Applications to Chemistry (Frontiers in Chemistry, Vol. 14). Edited by R. E. Burk and Oliver Grummitt. Published under the auspices of the Western Reserve University and by Interscience Publishers Inc., 1946, pp. 151 + xii. Price \$ 3.5.

This book is a compilation of a series of lectures delivered by several outstanding scientists in the realm of Chemistry and Physics at the Western Reserve University. They were intended to convey to graduate students "the flow of chemical research, and for keeping industrial chemists abreast of their science." The publication of these lectures in book form makes them available to a wider public, and forms a most welcome and notable contribution to a field in which there has been a distinct paucity of readable literature.

The treatise opens with a treatment of "Electron diffraction" by Dr. L. H. Germer. From the point of view of ordinary readers, perhaps a little more space should have been devoted to give a fuller information about the diffraction patterns and the experi-

mental technique behind them. The second article on the "Electron Microscope and its applications" by Prof. L. Marton is a remarkable contribution, embodying as it does, most of the salient features of the instrument with clarity and accuracy. Its worth can be equally appreciated both by the layman and the expert. Next follows a notable analysis of "X-ray diffraction and its applications" by Dr. Maurice L. Huggins. He has classified many of the latest photographic methods for the structure determination of complex molecules and for building trial crystal models therefrom. The next two succeeding chapters on "Chemical spectroscopy" and "Application of absorption spectra to chemical problems" come from the pen of Prof. W. F. Brode. He unfolds his theme from the basic elementary principles and covers adequately most of the wide range of his subjects, including the "internal-standard" method of quantitative analysis. The last chapter on the "Infra-red spectrometer and its application" by Dr. R. Bowling Barnes is a very useful contribution illustrating the identification of molecules by their infra-red spectrum.

Handsome in appearance and interspersed with excellent diagrams and wealth of information, the book should serve as an invaluable guide to research workers. The reviewer heartily congratulates the editors on their laudable effort and hopes that many similar treatises will rapidly follow in its wake.

S. D. C.

Advances in Colloid Science. Volume II. Scientific Progress in the Field of Rubber and Synthetic Elastomers. Edited by H. Mark and G. S. Whitby. Published by Interscience Publishers Inc., New York, 1946, pp. 453 + xii. Price \$ 7.0.

An up-to-date review of researches done on the various branches of natural and synthetic rubbers has been presented in this volume. There are nine chapters in the book dealing respectively with second order transition, crystallisation, X-ray studies, thermodynamics, viscous properties, elasticity, vulcanisation, photo-vulcanisation and reinforcing ingredients. Each chapter has been written by a specialist on the subject recording the present state of knowledge on the subject and indicating problems on which further information is desirable. We expect that the book will prove to be a great incentive to further research on natural and synthetic rubbers.

N. C. S. G.

Catalogue of Insectioides and Fungioides Vol. I. Chemical Insectioides. By Donald E. H. Frear. Published by Waltham, Mass: Chronica Botanica Co., 1947; Calcutta, Bombay and Madras: Macmillan and Co., Ltd, pp. 203 + xii. Price \$ 6.5.

In the midst of the most destructive War, it was announced that one of the goals of victory should be freedom from want, disease and other miseries of mankind. As a matter of fact chemotherapy in recent years has made a great stride towards that end by controlling the disease of man and contributing much towards other demographic trends. Much are to be done and more effective chemicals are to be produced with unprecedented potency that may help in controlling the disease not only in man but in domestic stock, in removing unwanted insects and fungi for better production of food

crops and in offering suitable preservatives for the safe storage of foodstuffs. The discovery of D.D.T., rotenone, organic thiocyanates and many other insecticides have contributed much towards the above ends and considerable interest is being shown for the production of still better and effective insecticides. Volumes of literature have already accumulated and it is practically impossible now to collect all the relevant data.

The publication of a catalogue of chemical insecticides at this moment has been most timely and would help the research workers in this field to a considerable extent. The catalogue has been broadly divided into 3 sections—list of various insecticides, author index and a patent list. The list of authors would be very useful for those already in the line; but one in India would miss the Indian Patents in the patent list. The main chapter is on the names of various insecticides (about 10,000) and their uses. A new system of classification has been followed. It would not be too difficult to follow the coding system from the explanatory notes given in the introduction, still a formula index as well as a list based on the mode of their uses at the end of the Catalogue would have been helpful to a casual reader. This might be incorporated in subsequent edition; but the catalogue seems to be indispensable for the libraries of the Institutes devoted to chemical, medicinal, agricultural, horticultural and public health work. In addition, it will be of interest to executives and others concerned with pest-control materials.

U. P. B.

ERRATA

Page 479, TABLE I (contd.)

In place of

17. Copper cystin $[\text{Cu}(\text{C}_6\text{H}_{10}\text{N}_2\text{O}_4\text{S}_2)] \cdot 2\text{H}_2\text{O}$
and 18. Copper bispyridine thiocyanate $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_2](\text{SCN})_2$

Read

17. Copper bispyridine thiocyanate $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_2](\text{SCN})_2$
and 18. Copper cystin $[\text{Cu}(\text{C}_6\text{H}_{10}\text{N}_2\text{O}_4\text{S}_2)] \cdot 2\text{H}_2\text{O}$.

Page 489, paragraph 2, line 4

Read "after 141°."

"It contained chlorine and the hydroxy group. (Found : Cl, 44.12. $\text{C}_{12}\text{H}_8\text{O}_2\text{Cl}_4$ requires Cl, 43.83 per cent). Chlorine in the side-chain was also estimated as AgCl. (Found : Cl, 33.23. $\text{C}_{12}\text{H}_8\text{O}_2\text{Cl}_4$ requires Cl, 32.87%) (assuming that all the hydrogen atoms in the side-chain have been replaced by chlorine). When the alkaline solution was acidified with dilute nitric acid a solid was obtained. It showed the presence of hydroxy and carboxy groups. It contained chlorine."

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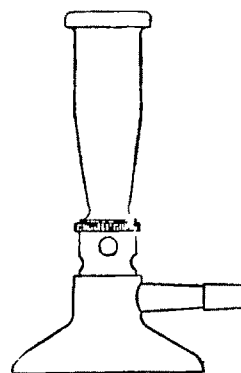
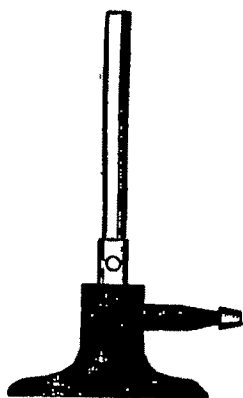
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